TECHNIQUE OF ORGANIC CHEMISTRY

Volume II

Catalytic, Photochemical, and Electrolytic Reactions

TECHNIQUE OF ORGANIC CHEMISTRY

ARNOLD WEISSBERGER, *Editor*

Volume I: Physical Methods of Organic Chemistry
In two parts

Volume II: Catalytic, Photochemical, and Electrolytic Reactions

Volume III: Heating and Cooling; Mixing; Centrifuging; Extraction and Distribution; Dialysis and Electrodialysis; Crystallization and Recrystallization; Filtration; Evaporating and Drying

Volume IV: Distillation

Volume V: Adsorption

Volume VI: Micro and Semimicro Methods

TECHNIQUE OF ORGANIC CHEMISTRY
Volume II

Catalytic Reactions

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Photochemical Reactions

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TECHNIQUE OF ORGANIC CHEMISTRY

INTRODUCTION

Organic chemistry, from its very beginning, has used specific tools and techniques for the synthesis, isolation, and purification of compounds and physical methods for the determination of their properties. Much of the success of the organic chemist depends upon a wise selection and a skillful application of these methods, tools, and techniques, which, with the progress of the science, have become numerous and often intricate.

The present series is devoted to a comprehensive presentation of the techniques which are used in the organic laboratory and which are available for the investigation of organic compounds. The authors give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling. It is hoped that the series will contribute to a better understanding and a more rational and effective application of the respective techniques. Reference is made to some investigations in the field of chemical engineering, so that the results may be of assistance in the laboratory and help the laboratory chemist to understand the problems which arise when his work is stepped up to a larger scale.

The field is broad and some of it is difficult to survey. Authors and editor hope that the volumes will be found useful and that many of the readers will let them have the benefit of their criticism and of suggestions for improvements.

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TECHNIQUE OF ORGANIC CHEMISTRY

GENERAL PLAN

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TECHNIQUE OF ORGANIC CHEMISTRY

PREFACE
to Volume II

The techniques for conducting catalytic, photochemical, and electrolytic reactions are discussed in the present volume.

Electrolytic and photochemical reactions have been used for a long time in preparative organic chemistry but have not found as wide an application as they might deserve. Apparatus for electrochemical work, though very simple, is available in relatively few organic laboratories. Photochemical reactions are employed in the organic laboratory in a rather haphazard way; their potentialities seem great, but at present systematic work is being done almost exclusively on biological photosynthesis and on the photolysis of very simple molecules. We hope that the chapters on electrolytic and photochemical reactions will demonstrate their merits and versatility and encourage their use.

There is no need for emphasizing the importance of catalytic reactions, and much ingenuity has been applied in the construction of special equipment. These apparatus, their operation, and the principles of catalyst preparation are discussed in the chapter on catalytic reactions. In many cases high pressures are employed, and the equipment developed for this purpose is equally useful for noncatalytic reactions under high pressure.

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CATALYTIC REACTIONS

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I. GENERAL PRINCIPLES

When the rate of a chemical reaction is influenced by the addition of a substance which appears neither as a reactant nor as a product, the phenomenon is known as *catalysis*. Reactions performed in the presence of such substances are called *catalytic reactions*. Substances exhibiting the phenomenon of catalysis are called *catalysts*. It is important to emphasize that under the definition of catalysts only material particles influencing the reaction velocity are understood. Thus, heat, light, electricity, or energy obtained from nuclear disintegration are clearly excluded.

Although the mechanism of catalysis has not been stated in a general theory covering the whole field it is probable that intermediate compounds (transition complexes) are always involved. Catalysts therefore influence reactions by changing the reaction path. More formally, catalysts influence the velocity of a reaction by lowering the energy of activation for given substances to react, thereby lowering the energy barrier which is involved in proceeding from reactants to products. The intermediate compounds formed between catalyst, reactants, and products represent a path of lower energy levels; as such, the velocity of the catalytic reaction is different from that of the uncatalyzed reaction.

In terms of thermodynamics a catalyst does not alter the free energy of a reaction since this change depends only upon the initial state of the reactants and the final state of the products. In other words, the catalyst does not change the equilibrium. If a reaction proceeds so slowly that it is only observed in the presence of a catalyst, for all practical purposes, a catalyst can be considered as initiating a new reaction.

Even more important than the ability to initiate and speed reactions is the property of specificity. When several reactions are possible, the catalyst is able to select and direct the course of the reaction in a specific path. Thus, an important characteristic of a catalyst is to produce a desired product, when many possibilities exist.

Although theoretically the catalyst appears in the products of the reaction in an unchanged form and should possess its initial activity for catalyzing more reactants, in practice, most catalysts undergo changes in some degree by combining with reactants or products. Such partial or complete loss in activity is called *poisoning.* In most of the cases the initial catalytic activity can be restored by a process of *regeneration.* If combination between catalyst and reactants or products is sufficiently large, it naturally might change the energy distribution of the system and cause changes in equilibrium.

For all practical purposes, the catalyst can: (*1*) increase the velocity of a reaction; (*2*) direct the reaction toward a specific product; (*3*) eliminate undesired side reactions; and (*4*) initiate a new reaction. In short, by means of catalysis, higher yields of a purer product in shorter reaction time become possible.

The domain of catalytic reactions may be classified according to the phase relationships between catalyst and substrate (reactants and products): in *homogeneous catalysis* catalyst and reactants occur in the same phase—gaseous, liquid or solid; in *heterogeneous catalysis* catalyst and reactants belong to different phases.

In the case of heterogeneous catalysis, various phase combinations of catalyst and substrate are possible. The following systems are most frequently encountered:

Catalyst	Substrate
(1) solid	gas
(2) solid	liquid
(3) liquid	gas
(4) liquid	liquid (immiscible)

Combinations (1) and (2) are usually called *contact catalysis.*

With solid catalysts, the adsorption of reactants upon the *catalyst surface* may be a major step in heterogeneous catalytic reactions. The adsorption brings the reactants into the active sphere of influence of the catalytic surface. In such cases, it was soon realized that the method of catalyst preparation greatly influences their activity. This in turn led to the development of *mixed catalysts.* Mixed catalysts are comprised of two or more chemical compounds. Although an exact understanding of the improved catalytic activity of mixed catalysts is still lacking, there are at least three phenomena which have been identified: (*1*) the increase of available surface; (*2*) the stabilization of the catalyst particle against crystal growth and sintering due to high temperature; and (*3*) the creation of a favorable orientation of the surface particles.

There is definite evidence that the surface of a solid catalyst does not possess uniform activity. The best indication of this is the frequently observed poisoning of a solid contact catalyst by a poison which is present in an amount sufficient to cover only a fraction of the total surface. This phenomenon can find a plausible explanation if it is postulated that only part of the catalyst surface is catalytically active. Such active parts are called *active centers* although their nature is still a subject of much speculation.

There are two terms used throughout the literature of catalysis which require explanation—*carrier* and *promoter.* The carrier, or support, is a catalytically neutral substance upon which the actual catalyst is deposited. The carrier serves only as a support for the catalyst and is in itself not active in the given reaction. Its role is to create and maintain a large, active surface for the catalytic substance.

The term promoter is used quite loosely throughout catalysis literature. In general, promoters are substances which enhance the activity of catalysts. They are not catalytically neutral and usually exhibit some activity in speeding the reaction in question. However, in combination with the catalytic substance, the combined action is not additive but is substantially greater than would be predicted.

There are various attempts to explain the action of promoters. Some theories depend entirely upon the properties of the catalytic surface and its improvement by promoters. Explanation of promoter action based on kinetics and reaction mechanisms are also known. A precise understanding of all these phenomena can be achieved only after systematic studies of surface, particle size, crystal structure, and crystal orientation of the catalyst, as well as of the mechanism and kinetics of the reaction.

Recently another concept was introduced into the literature of catalysis, namely, *complex-action* catalysts, *i.e.*, mixed catalysts which are comprised of two or more catalytic substances each capable of catalyzing a particular reaction.

For a more detailed discussion of the above principles, reference may be made to current literature.[1–6]

II. CATALYSTS AND THEIR PREPARATION

Most organic reactions involve catalytic effects of some kind and almost every chemical compound or mixture of compounds will catalyze a particular reaction to a greater or lesser degree. In order to limit the discussion, the present section will consider as catalysts only those substances which produce a specific, practical result that cannot ordinarily be achieved in the absence of a catalyst.

Many catalysts (*e.g.*, aluminum halides, hydrogen fluoride, sulfuric acid, and phosphoric acid) are prepared merely by following necessary steps to produce a material of high purity. For such catalysts, standard references on the preparation of chemical compounds should be consulted. Precautions should be taken to preclude contamination during catalyst preparation or storage of the completed catalyst. Similarly, all reactants which come into contact with the catalyst should be carefully purified to avoid poisoning of the catalyst. Consideration must be given also to possible deactivation of the catalyst by the products of the reaction.

---

[1] Corson, *J. Chem. Ed.*, **24**, 99, 150 (1947).

[2] Grosse, *Ind. Eng. Chem.*, **35**, 762 (1943).

[3] Komarewsky, *J. Chem. Ed.*, **19**, 563 (1942).

[4] Komarewsky, Riesz, and Thodos, *J. Am. Chem. Soc.*, **61**, 2525 (1939).

[5] Russell, *J. Chem. Ed.*, **22**, 163 (1945).

[6] Taylor, *Am. Scientist*, **34**, 553 (1946).

1. Preparation of Solid Catalysts

The most important, and least understood, group of catalysts are solid catalysts requiring development of specific surface properties to produce highly active catalysts. In consequence, the preparation of solid catalysts involves primarily the production and enlargement of the surface according to the demands of the specific reaction.

The requirements of a laboratory catalyst and an industrial catalyst are somewhat different. In the laboratory, the chief interest is in high activity and specificity in order to obtain the best yields of pure product. In industrial practice, cost of ingredients, catalyst life, physical strength, resistance to thermal shock, simplicity of preparative methods, ease of regeneration, and resistance to poisoning are factors which must be considered in addition to activity and specificity.

The requirement of the research catalyst for high activity and specificity can be achieved by preparing a contact with a highly developed surface. The production of a large amount of surface results from the creation of small particle size within the catalyst and possibly favorable orientation of crystals (active centers). These requirements may serve as guides in the selection of procedure and methods for the preparation of catalysts in laboratory practice. The following procedures (A to E), commonly used in the laboratory preparation of solid catalysts, are arranged in the probable order of increasing activity and specificity. In addition special procedures (F to I) are given for use under specific circumstances.

A. NATURAL CATALYSTS

Few natural products are found which possess high enough activity to be used as catalysts. However, some natural clays, bauxites, and diatomaceous earths have been used in catalytic work. As an example, the following natural clays (page 7) consisting of practically pure montmorillonite were found to possess some activity when used for the catalytic cracking of hydrocarbons.

In most cases a natural product must undergo chemical and physical pretreatment to render it suitable for use as a catalyst. Thus, acid-treating of diatomaceous earth, bauxite, and other natural products is used to remove iron and other undesirable constituents. The leaching of acid-soluble constituents provides increased catalyst sur-

Analysis	Clay number	
	(1)	(2)
Moisture	4.91	8.00
SiO_2	60.16	59.17
Al_2O_3	19.88	19.08
Fe_2O_5	2.98	2.79
FeO	0.54	0.42
TiO_2	0.08	0.13
P_2O_5	0.01	0.01
CaO	0.67	0.48
MgO	2.20	2.12
Na_2O	2.60	2.38
K_2O	0.40	0.36
Ignition loss	5.58	4.74
Sulfur		0.32

face. Heating to remove free and combined water also increases the catalyst surface and activity.

As an example, 200 g. of clay (1) was stirred in 2 liters of distilled water and was then treated with 100 ml. of concentrated sulfuric acid. The slurry was heated on a water bath for 2 hours, filtered and washed 3 times with distilled water, and finally dried at 105°C. The dried mass was screened and the 8–10 mesh fraction was collected. The sized particles were heated at 500°C. for 48 hours in a stream of nitrogen.

Activated clay prepared as described above produced 21% of gasoline from a Pennsylvania gas oil at a temperature of 500°C. and a liquid space velocity of 4.0 per hour. The same clay without activation produced only 5% of gasoline at the same conditions.

B. IGNITED CATALYSTS

A simple method of preparing catalysts is by decomposition of a thermally unstable chemical compound. For this purpose a nitrate or chloride is in general preferred as a starting material. The sulfates are usually to be avoided because of the higher temperatures needed for decomposition. The choice of other metal salts such as phosphates, bromides, iodides, etc., will depend upon availability and cost of such materials. Organic derivatives, such as formates, oxalates, and acetates, if available, are particularly valuable because not only do they decompose at low temperatures but also the metal is frequently reduced simultaneously, a necessary step in the preparation of certain catalysts, *e.g.*, nickel hydrogenation catalysts.

Metallic salts of complex acids are frequently used as a source of metal oxide mixtures. Such acids occur with elements in the fifth, sixth, and seventh groups of the periodic system. Thus, metallic chromates, tungstates, molybdates, manganates, and vanadates may be decomposed to produce mixed oxides.

C. IMPREGNATED AND IGNITED CATALYSTS

A widely used method of catalyst preparation consists of impregnation followed by ignition. The impregnation of the catalytic substance is performed by soaking a carrier in a concentrated solution of the catalyst salt. For example, a refractory carrier, such as china clay, bauxite, or alumina, is soaked in a concentrated solution of nickel nitrate. Following this impregnation, the catalyst is heated in a stream of nitrogen to remove nitrogen oxides and leave a nickel oxide in the refractory support. If desired, this catalyst can be subjected to the action of hydrogen to produce reduced nickel. Such a catalyst comprising 5 to 15% by weight of nickel can be used for the re-forming of hydrocarbon gases with steam to produce carbon oxides and hydrogen. If kieselguhr or diatomaceous earth is used as the support, sufficient nickel is impregnated to produce a final catalyst composition of 65% nickel and 35% kieselguhr by weight; after reduction, an active hydrogenation catalyst is obtained.

As another example of this preparation method, platinum foil or wire is dissolved in *aqua regia* and is evaporated to dryness. The solid is redissolved in concentrated hydrochloric acid, is again evaporated to dryness, and finally is dissolved in a small amount of water. This solution is impregnated into activated alumina (8–10 mesh or ⅛-inch pellets) to produce a catalyst which, after drying and reduction contains about 5% by weight of platinum. This is an active hydrogenation catalyst for olefins and benzene at 100–200°C. and atmospheric pressure, while at 300–350°C. it becomes active for dehydrogenation of cyclohexane to benzene.

Platinized and palladized carbons are prepared by evaporating a mixture of chloroplatinic acid or palladium chloride with charcoal. The residue is heated to 110–120°C. with occasional stirring; after cooling, hydrazine hydrate solution is added, the solution is cooled to −5°C. and made alkaline with sodium hydroxide solution.

D. PRECIPITATED CATALYSTS

One of the most widely used methods of catalyst preparation is that in which the active catalyst is precipitated as an insoluble material which, after washing free of extraneous ions, is converted into the final catalyst. The crystal size and activity of the end product will depend upon the conditions of precipitation, *i.e.*, concentration of solutions, order and rate of mixing solutions, temperature of precipitation, washing, drying, and subsequent thermal treatment.

Two examples of precipitated catalyst are presented for illustrative purposes. The preparation of chromic oxide gel by Frey and Huppke[7] produces an active paraffin hydrocarbon dehydrogenation catalyst. Chromic nitrate hydrate (800 g.) is dissolved in 8 liters of distilled water and is filtered to make a clear solution. To the above solution is added 400 g. of ammonium acetate in 16 liters of water. To the mixture at 50–60°C. is added, with stirring, about 8 liters of water containing 650 ml. of concentrated ammonium hydroxide (28% NH_3). After 2 hours, the precipitate is filtered and washed 3 times with hot water (30 liters). The precipitate is air dried at 50°C. After crushing and screening to 10–40 mesh, the catalyst is dried *in vacuo* for 8 hours, raising the temperature gradually to 250°C. The final reduction takes place in a hydrogen stream at temperatures up to 400°C. This catalyst is suitable for the dehydrogenation of gaseous alkanes, including ethane, propane, isobutane, and normal butane at temperatures of 350° to 500°C.[7]

A second example of a precipitated catalyst is a thoria aerogel prepared by Kistler, Swann, and Appel.[8] Thorium nitrate hydrate (50 g.) is dissolved in water and treated in the cold with excess ammonium hydroxide. The precipitate is washed with water by decantation until free of ammonium hydroxide. A slurry is made up to 600 ml. volume, is heated to 90°C., and is peptized by the addition of 5 g. of thorium nitrate hydrate with rapid stirring at 90°C. for 1 hour. After cooling to 60–70°C., the peptization is continued for another hour. The sol is transparent, orange yellow and is dialyzed for 24 hours. To concentrate to a content of 33–35% thorium oxide, the mass is evaporated in a vacuum steam bath. After cooling, a 10% solution of citric acid in alcohol is added with stirring to form a viscous solution which sets to a gel on standing. The gel is covered with acetone for 4 days, changing acetone daily. The gel in lumps is transferred to another beaker and let stand with fresh acetone for 24 hours more. Next, acetone is replaced by methanol for 12 hours and then the gel is placed into an autoclave and heated with methanol to about 250°C. From the resulting aerogel, 20-mesh particles are transferred to a catalyst tube and heated in air up to 430°C. This catalyst was used for the conversion of acetic acid to acetone. At 300°C. and a liquid space velocity of 8.0 volumes of acetic acid per hour per volume of catalyst, a 99.9% conversion of acid to acetone took place.

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[7] Frey and Huppke, *Ind. Eng. Chem.*, 25, 54 (1933).

[8] Kistler, Swann and Appel, *Ind. Eng. Chem.*, 26, 388–391 (1934).

E. COPRECIPITATED CATALYSTS

For the most effective preparation of catalysts, the coprecipitation method is recommended. This method, by virtue of simultaneous precipitation of catalyst and carrier, leads to a disperse catalyst of high activity. Whereas it may be expedient to produce catalysts by other methods, it is believed that coprecipitation will produce the most active form of catalyst without exception.

Two examples of coprecipitated catalysts follow. A nickel–alumina catalyst is prepared by initially forming a solution of sodium aluminate from aluminum nitrate and sodium hydroxide. Nickel nitrate plus additional nitric acid sufficient exactly to neutralize the sodium aluminate is prepared in a second solution. Upon adding the nickel nitrate - nitric acid solution to the sodium aluminate solution, the hydroxides of nickel and aluminum are precipitated simultaneously. The precipitated catalyst is washed free of anion, dried, and is pilled. The composition of reagents is chosen so that the catalyst after reduction contains 25% nickel and 75% alumina by weight. This catalyst produces complete dehydrogenation of cyclohexane to benzene at 300°C. and a liquid hourly space velocity of 0.3 (atmospheric pressure).

A second coprecipitation catalyst, comprising chromium and aluminum oxides, is prepared in a similar fashion. In this case an excess of sodium hydroxide is added to chromium nitrate to form sodium chromite while similar treatment of aluminum nitrate produces sodium aluminate. After mixing, addition of the theoretical quantity of nitric acid for neutralization coprecipitates the hydroxides. After washing and drying, the catalyst is pilled.

A catalyst comprised of 25% chromium oxide and 75% aluminum oxide was suitable for the reforming of gasoline fractions. Thus, a 70–150°C. fraction of Pennsylvania straight-run gasoline with an octane number of 49 was converted to 85% of a reformed gasoline with an octane number of 73. Reaction conditions were: temperature, 475°C.; atmospheric pressure; and a liquid hourly space velocity of 0.25.[9]

F. SKELETON CATALYSTS

The first special catalysts to be considered are of the type designated as alloy skeleton catalysts. In this preparation, metal in highly active state is produced by leaching out one metallic constituent from an alloy leaving a skeleton structure of the desired metal. The most widely known catalysts of this type were originated by Raney.[10] The catalyst is prepared by alloying equal weights of metal and aluminum and then dissolving the latter with aqueous sodium hydroxide. Catalysts have been prepared with nickel, cobalt, and iron, as well as combinations of silicon with cobalt or nickel.[11]

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[9] Komarewsky and Riesz, *Oil and Gas J.*, 42, No. 7, 90–93, 119 (1943).

[10] Raney, U. S. Pat. 1,628,190 (1927).

An example of Raney iron is given below.[12] To iron melted in a magnesia-lined induction furnace is added four times its weight of aluminum rod to make a 20% iron alloy. The alloy in 150-g. portions is pulverized and added in small portions to a solution of sodium hydroxide (250 g./l.) in a period of 3 hours. The temperature of the solution is maintained at 80–90°C. until cessation of hydrogen evolution. The alkali treatment is repeated, following which the residual material is washed with hot water by decantation until free of alkali. Water is removed by washing with absolute alcohol. The catalyst is stored under alcohol.

G. COLLOIDALLY DISPERSED CATALYSTS

Colloidally dispersed catalysts are generally prepared in the presence of protective colloids and are frequently used for the hydrogenation of organic compounds, especially when only small quantities of material are involved. Paal used sodium lysalbate[13] or protalbate[14] in preparing colloidal platinum catalysts. Skita[15] utilized gum arabic as a protective colloid.

A more recent example of this catalyst type is prepared by the PVA (polyvinyl alcohol) procedure of Rampino and Nord.[16] To 12.5 ml. 2% aqueous polyvinyl alcohol, are added 11 ml. water and 1 ml. palladium chloride solution (1% Pd). This is followed by dropwise addition of 0.5 ml. of a 4% solution of sodium carbonate. This step converts the palladium into hydroxide and neutralizes the liberated hydrogen chloride. Sufficient absolute alcohol is added to produce a 50% water–alcohol mixture. The brown colloid is transferred to the hydrogenation flask and shaken under hydrogen atmosphere to reduce the palladium. The catalyst is then ready for use as a hydrogenation catalyst.

Quinone can be reduced in acid solution by use of the Pd–PVA catalyst.[17] The reaction mixture consisted of 1.08 g. quinone and 0.25 ml. concentrated hydrochloric acid in 50 ml. 50% alcohol catalyst solution containing 10 mg. palladium and 250 mg. PVA (du Pont RH-391). Absorption of hydrogen at the end of ten minutes was 95 ml.

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[11] Komarewsky, Riesz, and Estes, *The Fischer-Tropsch Process*. American Gas Association, New York, 1945, pp. 29–30.

[12] Thomson and Wyatt, *J. Am. Chem. Soc.*, **62**, 2555 (1940).

[13] Paal, *Ber.*, **37**, 126 (1904).

[14] Paal, *Ber.*, **38**, 1401 (1905).

[15] Skita, *Ann.*, **427**, 255–280 (1922); **431**, 1–20 (1923).

[16] Rampino and Nord, *J. Am. Chem. Soc.*, **63**, 2745 (1941).

[17] Rampino and Nord, *J. Am. Chem. Soc.*, **63**, 3268 (1941).

H. METAL FILM CATALYSTS

Films of active metal can be applied to surfaces by evaporation of metal from a wire although such catalyst forms are rarely applied in practice. Layers of iron may be prepared by evaporation, sodium chloride being evaporated simultaneously to prevent sintering of the iron.[18] Metallic layers can also be prepared by means of the sputtering which occurs by impact of high speed ions with the cathode in an electrical discharge.[19]

Beeck, Smith, and Wheeler[20] have developed an evaporation procedure which produces films of uniform high activity. The glass vessel is baked under high vacuum for at least 2 hours at or close to 500°C. The metal filament must also be freed of occluded gases by heating just below the evaporation point for the last hour during the baking-out process. After cooling, metal is evaporated to the cooled glass surface at the rate of approximately 0.5 mg. metal per minute. It was found that catalyst films evaporated in the presence of gases (*e.g.*, 1 mm. nitrogen or argon) were many times more active than films prepared under high vacuum.

I. METAL WIRE AND FOIL CATALYSTS

Metals can sometimes be used as catalysts in the form of wire or foil. When so used, they are usually in a low state of catalytic activity and some type of pretreatment is necessary to obtain a maximum catalytic effect. This activation is usually connected with an increase in the available surface area of the catalyst. Thus, a nickel wire is rendered active for the hydrogenation of ethylene by alternate oxidation and reduction at 600°C.[21] For platinum wire or foil hydrogenation catalysts, the catalytic activity can be improved by electroplating in a solution of chloroplatinic acid.[22]

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[18] Frankenburger and Mayerhofer, *Z. Electrochem.*, **35**, 590 (1929).

[19] Bredig and Allelio, *Z. physik. Chem.*, **126**, 41 (1927).

[20] Beeck, Smith, and Wheeler, *Proc. Roy. Soc. London*, **A177**, 62–90 (1940).

[21] Farkas, Farkas, and Rideal, *Proc. Roy. Soc., London*, **A146**, 630 (1934).

[22] Farkas and Farkas, *Trans. Faraday Soc.*, **33**, 678, 837 (1937); *J. Am. Chem. Soc.*, **60**, 22 (1938).

2. Forming of Solid Catalysts

The shape or form of the catalyst will depend greatly upon the reaction involved, the nature of the catalyst and its preparation and upon the scale of the reaction. In general, solid catalysts are received either as a wet mass or in the form of a dry powder. For laboratory work it is usually convenient to dry the wet mass received as a filter cake at 105–110°C. in such a way as to receive large pieces. The dried pieces are then crushed carefully and screened. It is best to select a narrow size range, *e.g.*, the material passing an 8-mesh screen but retained by a 10-mesh screen is convenient for laboratory application. This procedure is wasteful of material but is usually justified in experimental work where only small amounts of catalyst are required.

A second procedure is to extrude the wet catalyst paste as a string of desired diameter. The pieces can be formed by cutting the wet strings or by careful grinding after drying. An alternative procedure is to dry the catalyst, grind to a very fine powder, and then wet to a paste of appropriate consistency. In either case allowance must be made for shrinkage upon final drying and heating of the catalyst.

A procedure which can be applied to almost all forms of solid catalysts is the use of high compression of a fine powder in a pilling or tabletting device. Automatic machines such as those used in the pharmaceutical industry for making pills can be employed for the purpose.[23] It is usually necessary to add a small quantity of material (approximately 1%) to lubricate the compression of the powder. Lubricants must be selected which have no deleterious effect upon the activity of the catalyst; aluminum fatty acid soaps, such as the stearate, or graphite are usually satisfactory for this purpose. Wood flour, starch, dextrose, etc., can be added to the mixture to obtain increased porosity of the final pill. The moisture content of the pill, the fineness of grinding, the pressure of formation, the lubricant and the filler used are all details which must be determined empirically. The catalyst is customarily in the shape of cylinders of about equal length and diameter. Special forms such as Raschig rings, Berl saddles, rounded-end cylinders, balls, and other forms also can be prepared.

Catalysts for catalytic cracking have been prepared in the form of hard, translucent spheroids (3 mm.) by means of a highly specialized procedure. A hydrogel prepared from solutions of sodium silicate and aluminum sulfate is passed as strings into a layer of light mineral oil floating above a bottom layer of water. This operation produces droplets of the gel or so-called "beads." After washing and drying, the beads shrink to about 1/11 of the original volume. Catalytic cracking catalyst is produced which is comprised of 89.5% SiO_2, 10.0% Al_2O_3, and 0.5% H_2O and which possesses a pore surface area[24] of 420 sq. m./gram.

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[23] F. J. Stokes Machine Co., Philadelphia, Pa.

3. Dimensions of the Catalyst Particle

Thiele[25] showed by means of mathematical considerations that below a certain particle size, the activity of a porous catalyst is proportional to the amount present. If the grain size is increased much above this value, the catalytic activity will depend upon the total external surface of the granules. The value dividing the two regions is determined by a dimensionless modulus, $X_s\ (c/rk)^{\frac{1}{2}}$ where X_s is the radius of the equivalent sphere, c is the activity of unit internal surface of the pores, r is the hydraulic radius of the pores, and k is the diffusion coefficient. With consistent units the transition values of the modulus do not differ greatly from unity.

Another approach to the proper size of granule is obtained by consideration of the heat transfer to gases flowing in turbulent motion through packed tubes. Leva[26,27] determined theoretically and experimentally that at a ratio of granule size to reaction diameter of 0.15 a maximum coefficient of heat transfer occurs. This relationship is a valuable guide in selecting sizes of catalyst granules for a given tube diameter.

The preferred form of catalyst should be such that the ratio of maximum to minimum dimension does not exceed 3:1 and preferably should be close to 1:1. This specification will minimize any tendency of the catalyst granules to lie flat one upon the other which would reduce effective contact with the gas stream. The ideal catalyst would be spherical in shape.

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[24] Porter, *Chem. Met. Eng.*, **53**, 94–8 (1946).

[25] Thiele, *Ind. Eng. Chem.*, **31**, 916–920 (1939).

[26] Leva, 110th Meeting of the American Chemical Society, Division of Industrial and Engineering Chemistry, 1946.

[27] Leva, Weintraub, Grumer, and Clark, 111th Meeting of the American Chemical Society, Division of Industrial and Engineering Chemistry, 1947.

4. Activation of Catalysts

The final step in the preparation of the catalyst is the conversion of the catalyst granules into the active state required by the particular reaction. For example, the last step in the formation of a hydrogenation catalyst would be the reduction of the oxide to the metallic state. Other catalysts might require pretreatment with inert gas, oxygen, hydrogen sulfide, or carbon monoxide to form dehydrated, oxidized, sulfided, or carbided catalysts, respectively. If the reaction used to form the active surface is exothermic, care must be taken to avoid overheating. This can be accomplished by beginning the activation at low temperature. It is often advisable to dilute the activating gas to avoid local overheating of the catalyst surface.

5. Reaction Time

In batch reactions, reaction time is measured as the elapsed time interval at a particular temperature. In flow homogeneous reactions it is convenient to express time in terms of *volume space velocity*, *i.e.*, the volume of feed, measured at standard conditions, per unit time per unit volume of reactor. This unit has the dimension of reciprocal time and is commonly expressed on an hourly basis. Care must be taken that the standard conditions are clearly stated, since the charge may be liquid in some cases and gaseous in others.

For flow heterogeneous reactions, the use of volume space velocity as defined above has also been employed. However, expression of the time factor in terms of a *weight space velocity* has been found valuable in making correlations, *i.e.*, the weight of feed per unit time per unit weight of catalyst.

Space-time-yield is a term frequently encountered in catalytic processes of the flow type. It is defined as the yield of a desired product in unit time per unit volume of catalyst. In general the space-time-yield increases with increasing space velocities, but above some particular value, the space-time-yield becomes independent of space velocity and approaches a constant value. Space velocity and space-time-yield are of prime importance in determining the size of the industrial catalytic chamber for a given reaction.

III. LABORATORY TECHNIQUES IN CATALYSIS

The present chapter is devoted to the laboratory techniques of catalytic reactions and emphasizes basic procedures and equipment used in performing catalytic reactions in organic chemistry. The equipment and methods described are not necessarily the only ones available but constitute techniques which have been checked and are in general use in many laboratories. Although the discussion is limited to laboratory scale installations, some of the equipment, particularly of the constant flow type, might be considered as being of pilot plant dimensions.

The laboratory techniques used in performing catalytic reactions in organic chemistry have been organized on the basis of the pressure employed, namely, atmospheric, subatmospheric, and superatmospheric pressure. For each pressure range, batch and flow procedures are presented. While laboratory techniques might be systematized in other ways, *e.g.*, on the basis of homogeneous or heterogeneous phase catalysis, the present method provides maximum flexibility in selection of techniques and catalysts.

Although this chapter gives laboratory techniques involved in performing catalytic reactions, it does not include methods for investigation of catalysts or reaction mechanisms, *e.g.*, surface structure of catalysts or kinetics of catalytic processes. Likewise, no attempt is made to list catalysts suggested in the literature or to review reactions to which catalysis has been applied. The bibliography of books at the end of this chapter indicates the scope of such an undertaking and may also serve as a guide to the reader. However, a few of the most important reactions are discussed in some detail to illustrate specific techniques.

Although the chapter is designed to present catalytic reaction techniques, many of the methods described are of such a character that they are applicable to noncatalytic processes. This is particularly true of the *high pressure apparatus and methods*. Some catalytic reactions, *e.g.*, esterification and saponification, can be carried out satisfactorily in standard laboratory glassware and such techniques are treated only briefly in the present chapter. For a detailed discussion of stirring, the reader is referred to the chapter by Rushton.[27a]

1. Catalytic Reactions at Atmospheric Pressure

A. BATCH SYSTEMS

The usual techniques of the organic chemist can be applied to batch catalytic reactions at atmospheric pressure. The common arrangement of a three-necked, mercury-seal stirrer apparatus can be used with solid or liquid catalysts. For introduction of gaseous reactants a gas inlet tube placed at the bottom of the vessel is desirable; to aid dispersion of the gas into fine bubbles, a sintered glass disk in the gas inlet tube is useful. An example of the application of the above principles is the apparatus shown in Figure 1.[28] The special curved walls of the stirring vessel serve to prevent splashing and to return the catalyst to the agitated liquid zone. Flasks provided with vertical baffles are particularly efficient for providing thorough mixing of catalyst and reactants.

[27a] Rushton, "Mixing," this series.

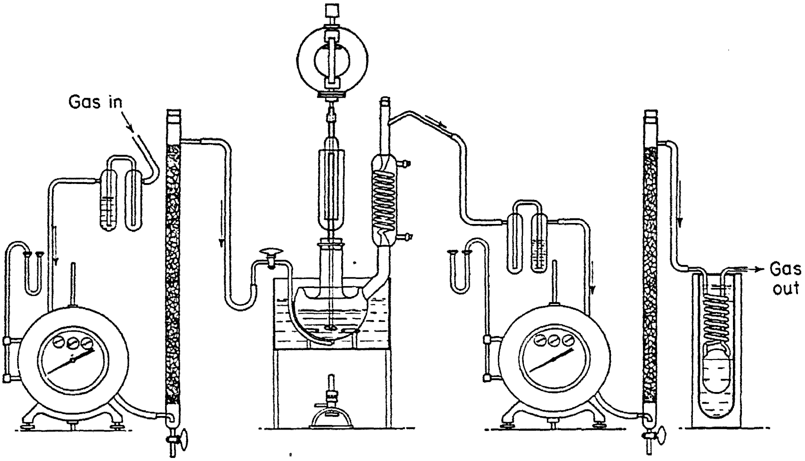

Fig. 1. Stirring apparatus for catalytic polymerization.[28]

The apparatus shown in Figure 1 can be employed for the polymerization of propylene in the presence of liquid phosphoric acid catalyst. With a reaction flask of 1-liter size, 100 g. 100% phosphoric acid is used at a temperature of 130°C. Propylene is passed into the flask at the rate of 4.55 liters per hour. The conversion of propylene to liquid polymers is 83%.

Another application of the gas dispersion principle has been employed for the hydrogenation of small quantities of material (1 gram or less).[29] Fig. 2 shows a simple form of dispersion tube reactor, and Fig. 3 an improved type of hydrogenator.[30] Finely divided platinum or palladium catalysts are used as hydrogenation catalysts.

[28] Ipatieff and Corson, *Ind. Eng. Chem.*, 27, 1070 (1935).

[29] Cheronis and Koeck, *J. Chem. Ed.*, 20, 488–496 (1943).

[30] Cheronis and Levin, *J. Chem. Ed.*, 21, 603–609 (1944).

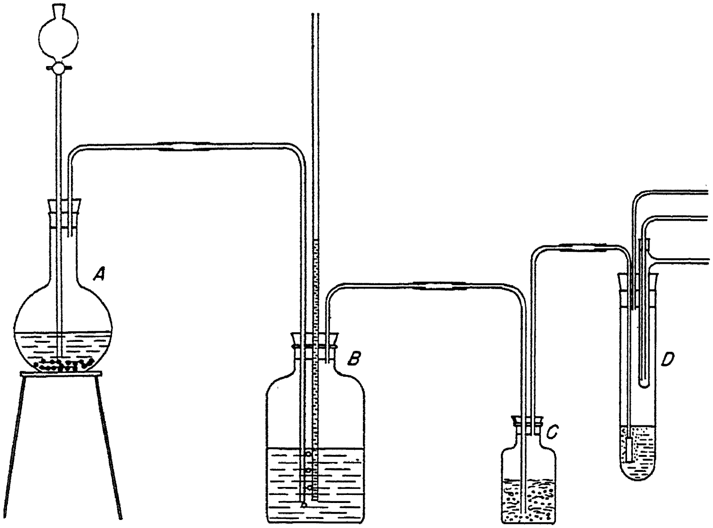

Fig. 2. Apparatus for semimicro hydrogenation.[29] *A*, hydrogen generator (zinc – sulfuric acid); *B*, wash bottle; *C*, calcium chloride drier and glass wool trap; *D*, hydrogenator.

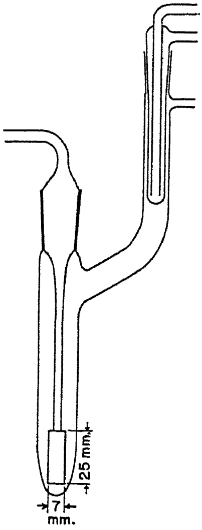

Fig. 3. Semimicro hydrogenator.[30]

It is frequently advantageous to reflux undecomposed material to the reaction vessel in order to obtain complete conversion. This principle is demonstrated by the equipment shown in Figure 4.[31] Vapors of the liquid boiled in the flasks are forced to pass over heated catalyst in the form of a wire where reaction takes place. Heat is supplied to the wire by the passage of electric current. Gaseous products flow past the reflux condenser but unreacted liquid is condensed and is returned by means of the liquid seal return tube.

In batch reactions where water is a by-product, a water-immiscible solvent, such as benzene, toluene, or carbon tetrachloride, can be used to aid in the removal of water. The apparatus illustrated[32] in Figure 5 is used if the solvent is lighter than water. It is a modified Vigreux-type column in which the liquids are condensed by a reflux condenser and, after gravity separation, the light nonaqueous portion is returned to the column by means of the lower side arm. A baffle in the return tube prevents carry-over of water droplets from the splashing of the refluxed liquids.

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[31] *Organic Syntheses*, Coll. Vol. II. Wiley, New York, 1943, p. 103.

[32] *Synthetic Org. Chemicals*, **15**, No. 3 (1943).

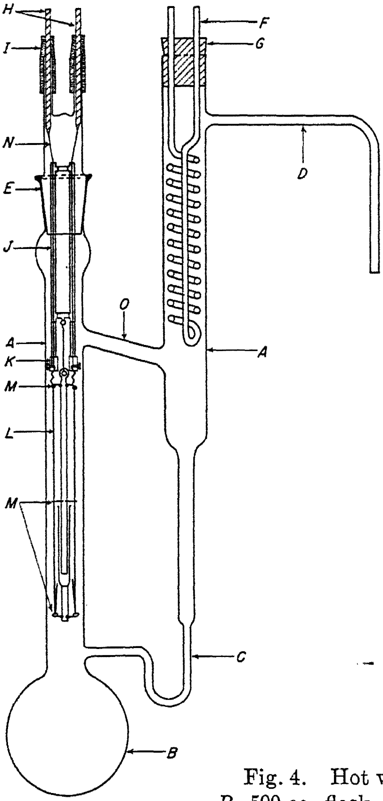

Fig. 4. Hot wire reflux reactor.[31] *A*, 32-mm. tubing; *B*, 500-cc. flask; *C*, 7-mm. tubing; *D*, 8-mm. tubing; *E*, No. 35 standard taper joint; *F*, coil of 3/16-in. copper tubing; *G*, cork stopper; *H*, 1/8-in. brass rod; *I*, rubber tubing; *J*, 3-mm. glass tubing; *K*, brass electrical connectors; *L*, Chromel C resistance ribbon No. 37 B and S gage, 1.9–2 ohms per foot, width 1/16 in., length 56–60 in.; *M*, tungsten wire-loop supports sealed into the suspended glass rod; the center supports are of 0.01-in. (diam.) wire; those at the top and bottom, of 0.015-in. (diam.) wire; *N*, copper wire No. 22 B and S gage; *O*, 12-mm. tubing.

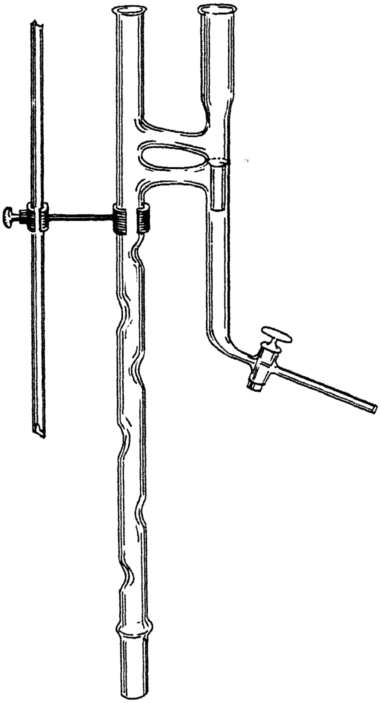

Fig. 5. Modified Vigreux column.[32]

One of the most valuable means for combined distilling-refluxing methods is provided in the Clarke and Rahrs column. A typical modification of this column is shown[33] in Figure 6A. While the reaction mixture is being refluxed, the water which collects in the side arm at the head of the distilling column is drawn off whenever necessary by means of the stopcock. This column is used when the boiling point of the azeotrope is lower than the boiling point of the reactants. For reactions in which one of the reactants is lower boiling than the azeotrope the modification shown in Figure 6B is employed.[34] The

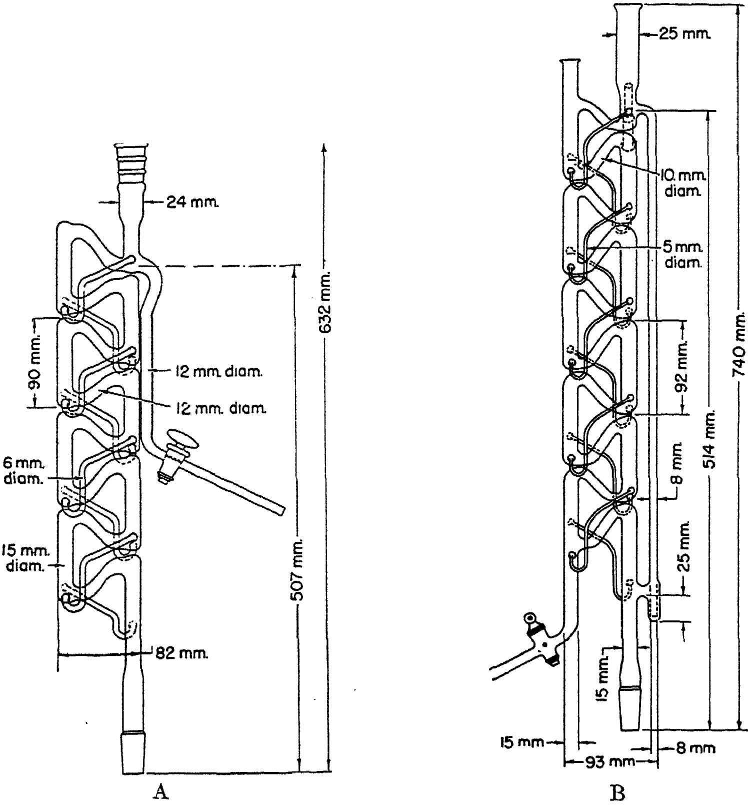

Fig. 6. Modifications of the Clarke and Rahrs column.

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[33] *Synthetic Org. Chemicals*, 9, No. 3 (1936); Figure Courtesy C. F. H. Allen.

[34] *Synthetic Org. Chemicals*, 11, No. 1 (1938); *Org. Syntheses*, 24, 72 (1944).

aqueous portion collects in the lower portion of the column and is withdrawn whenever necessary by means of the stopcock. A by-pass fitted with a trap serves to return extremely volatile reactants, *e.g.*, methyl alcohol, from the top of the column.

B. CONTINUOUS FLOW SYSTEMS

(1) Low-Temperature Flow Systems. The principle of stirring to obtain the required contact between reactants and catalyst is readily applicable to flow systems. For low-temperature work the apparatus of Pines, Grosse, and Ipatieff[35] is useful (Fig. 7). The reactor is desgned for the continuous withdrawal of catalyst-free liquid which is aiccomplished by centrifuging the liquid product in the stirring device itself. The catalyst is projected toward the side of the vessel while the clear liquid is raised through opening *E* of the hollow stirring shaft by means of nitrogen pressure. The liquid product is collected in tube *G* from a collecting tray (detail) and passes to stabilizer *H*. The application of this stirrer to a flow system used for the continuous alkylation of isobutane with olefins is shown in Figure 8. The liquefied mixture of gaseous hydrocarbons, kept in the charger, is precooled in *C* before passing to the reaction vessel. Hydrogen chloride, stored in a bomb, is added continuously while the aluminum chloride catalyst is charged to the reaction vessel prior to the run. Liquid products formed by the reaction are collected from the bottom of the stabilizer, while the stabilized gas and nitrogen pass through the remainder of the condensing and purification train.

With a charge consisting of 23.8% *n*-butenes (67% 2-butene, 33% 1-butene) and 76.2% isobutane being passed into the reactor at the rate of 300–325 ml. per hour, approximately 80 ml. per hour of liquid product was recovered. The catalyst was 15 g. of anhydrous aluminum chloride contained in the reactor while 1–4 g. per hour of hydrogen chloride was added continuously with the feed. The liquid product contained from 52 to 65% of octanes. The reactor temperature was maintained at −35°C.

(2) High-Temperature Flow Systems. The continuous flow system with a solid catalyst maintained at high temperatures is a fundamental technique in catalytic reactions and a fairly extensive treatment of this important subject is presented. The important phases of continuous processes to be considered are: (*a*) introduction of gases; (*b*) purification of gases; (*c*) metering of gases; (*d*) introduction of

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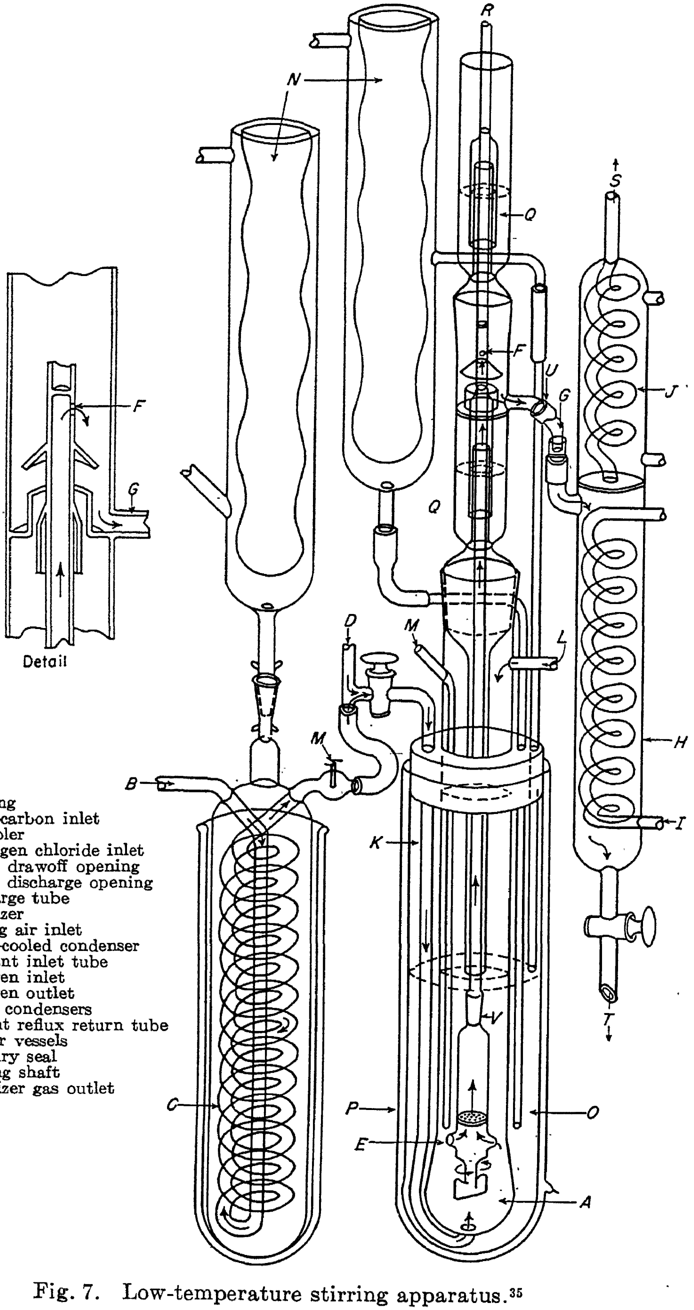
[35] Pines, Grosse, and Ipatieff, *J. Am. Chem. Soc.*, 64, 33–36 (1942).



A,	opening
B,	hydrocarbon inlet
C,	precooler
D,	hydrogen chloride inlet
E,	liquid drawoff opening
F,	liquid discharge opening
G,	discharge tube
H,	stabilizer
I,	cooling air inlet
J,	water-cooled condenser
K,	reactant inlet tube
L,	nitrogen inlet
M,	nitrogen outlet
N,	reflux condensers
O,	coolant reflux return tube
P,	Dewar vessels
Q,	mercury seal
R,	stirring shaft
S,	stabilizer gas outlet

Fig. 7. Low-temperature stirring apparatus.[35]

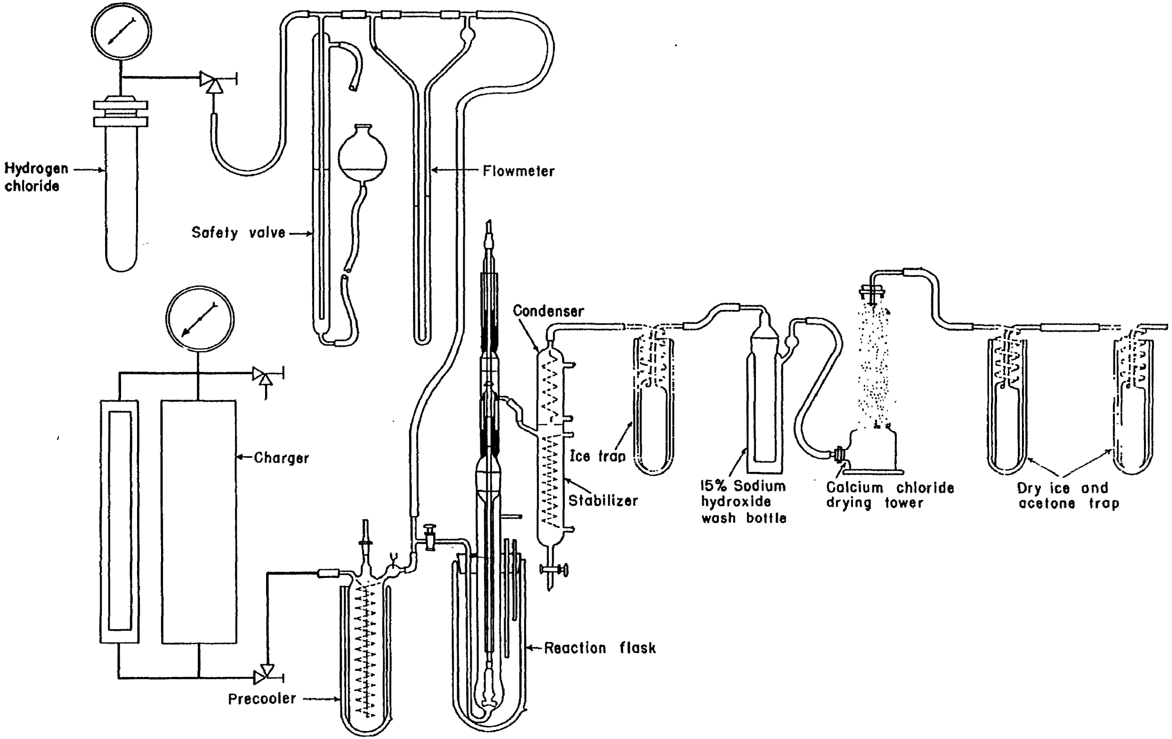


Fig. 8. Flow diagram of low-temperature continuous flow apparatus for alkylation of isobutane with gaseous olefins.[35]

liquids; (*e*) introduction of solids; (*f*) furnaces; (*g*) catalytic reactors; and (*h*) collection of products.

Introduction of Gases. It is generally possible to obtain the required gases under high pressure in gas cylinders, and it is only necessary to reduce the pressure for laboratory use. Needle valves may be employed. With this type of equipment, as the pressure in the cylinder drops, the gas rate will also drop. A single-stage reducing valve will deliver a set outlet pressure, or for fine adjustment of flow, a two-stage reducing valve plus a needle valve is recommended. If commercial gases are purchased, it is well to standardize if possible on one supplier to minimize the number of connectors required.

A number of precautions must be observed. A regulator used for oxygen should never be employed for any other service in order to avoid the danger of the formation of explosive peroxides. Gages and regulators should never be oiled for the same reason. Cylinders should never be moved without the valve protecting cap screwed in place since injury to the valve might cause the cylinder to act as a jet projectile. When in service, the cylinder should be chained in place securely. The general precautions for high-pressure work should be followed carefully.

Purification of Gases. For most purposes compressed gases such as hydrogen, oxygen, nitrogen, and carbon dioxide are sufficiently free from deleterious impurities that no further purification is necessary. However, it is well to dry the gases as a routine precaution. Depending upon the nature of the gas, an appropriate drying reagent is selected from the following: calcium sulfate, calcium chloride, barium oxide, activated silica gel, activated alumina, and phosphorus pentoxide, and special commercial preparations such as Drierite, Dehydrite, and others. See the chapter on evaporating and drying by Broughton.[35a]

In nitrogen, which is frequently used to purge the system from combustible gases, sufficient amounts of oxygen may be present to cause local overheating of the catalyst. If a gas analysis of nitrogen reveals 0.2% or more of oxygen, it is good practice to remove the oxygen by passage through alkaline pyrogallol solution or over reduced copper at 400°C. A relatively complete discussion of gas purification is given by Farkas and Melville.[36]

[35a] Broughton, "Evaporating and Drying," this series.

[36] Farkas and Melville, *Experimental Methods in Gas Reactions.* Macmillan, London, 1939, pp. 149–174.

Metering of Gases. The method selected for metering the gases entering the catalytic system will depend upon the accuracy required. For low flows where only a qualitative knowledge of the rate of gas flow is required, a simple bubbler is sufficient. The design shown in Figure 9 has proved satisfactory since it combines a safety trap in a simple, compact unit. For more accurate measurement of gas flow, a flowmeter of the fixed area type producing a pressure drop across a constriction may be employed. Alternatively, a variable area flowmeter may be used.[37] A positive displacement meter, either of the wet or dry type, may be used for precise measurement of gas quantities.

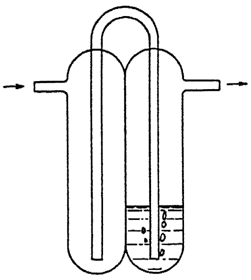


Fig. 9. Bubbler for estimation of low rates of gas flow.

Introduction of Liquids. For catalytic reactions involving the continuous feeding of a liquid reactant or reactants to the system, the rate of charging must be maintained constant. While certain reactions will tolerate minor variation, in general, the liquid must be charged at a relatively constant rate to obtain optimum yields with a minimum of secondary and undesirable reactions. The methods to be described by no means cover all the possibilities but are intended to present methods which have been found most useful in connection with catalytic reactions in the laboratory.

Capillary Feeder. If a liquid passes through a length of capillary tubing at a constant temperature and a constant pressure differential, the rate of feeding will remain constant. A simple device is shown in Figure 10, for use at atmospheric pressure. The capillary which regulates the flow of liquid is *D*; for most liquids a fine capillary is drawn out, coiled, and placed inside of a protecting jacket. If the room temperature is not constant, the capillary should be placed in a thermostat. When *A* is closed, the liquid which flows into the capillary must be replaced by air drawn in at *B*. This device tends to produce a constant liquid head relative to point *E* where the liquid enters the catalyst tube. The charging buret if calibrated by volume must be corrected by a constant factor because of the presence of the equalizing tube. A ground-glass connection at *C* permits various capillary tubes to be interchanged until a capillary of appropriate dimensions is found. A more flexible type of capillary feeder is that shown in Figure 11. In this type a Nichrome wire fits the glass capillary closely. Variation of feed rates can be made by changing the length of wire inserted in the capillary. A suitable buret is attached by means of a ground-glass joint, *e.g.*, a buret of the type illustrated in Figure 10.

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[37] Rotameters (Flowrators) are available from the *Fischer and Porter Co.*, Hatboro, Pa.

Pumps. Bellows pumps have been found well suited for the charging of low rates of liquid flow. The original design of the bellows pump[38] utilized a glass check valve assembly equipped with stainless steel balls. One of the best designs has been described by Corson and Cerveny[39] (Fig. 12). The main element is the flexible metal bellows which replaces the piston of the ordinary piston-type pump. Adjustment of flow rate is made by adjusting the stroke obtained by means of a small constant-speed motor, a gear reducer, and an eccentric with needle bearings. The pump (see Fig. 12) is designed for operation at 1 to 2 atmospheres gage and will deliver 5 to 2500 cc. of liquid per hour.[40] By suitable modification of the bellows, operation at 3 atmospheres can be obtained with a brass bellows while a stainless steel bellows can be used for 15 to 30 atmospheres.

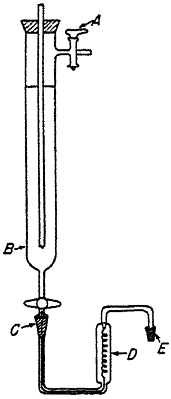

Fig. 10. Capillary feeder.

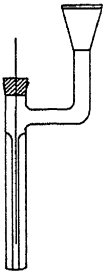

Fig. 11. Variable capillary feeder.

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[38] Tropsch and Mattox, *Ind. Eng. Chem., Anal. Ed.*, **26**, 1338 (1934).

[39] Corson and Cerveny, *Ind. Eng. Chem., Anal. Ed.*, **14**, 899–900 (1942).

[40] This pump is available from *Research Appliance Co.*, Pittsburgh, Pa.

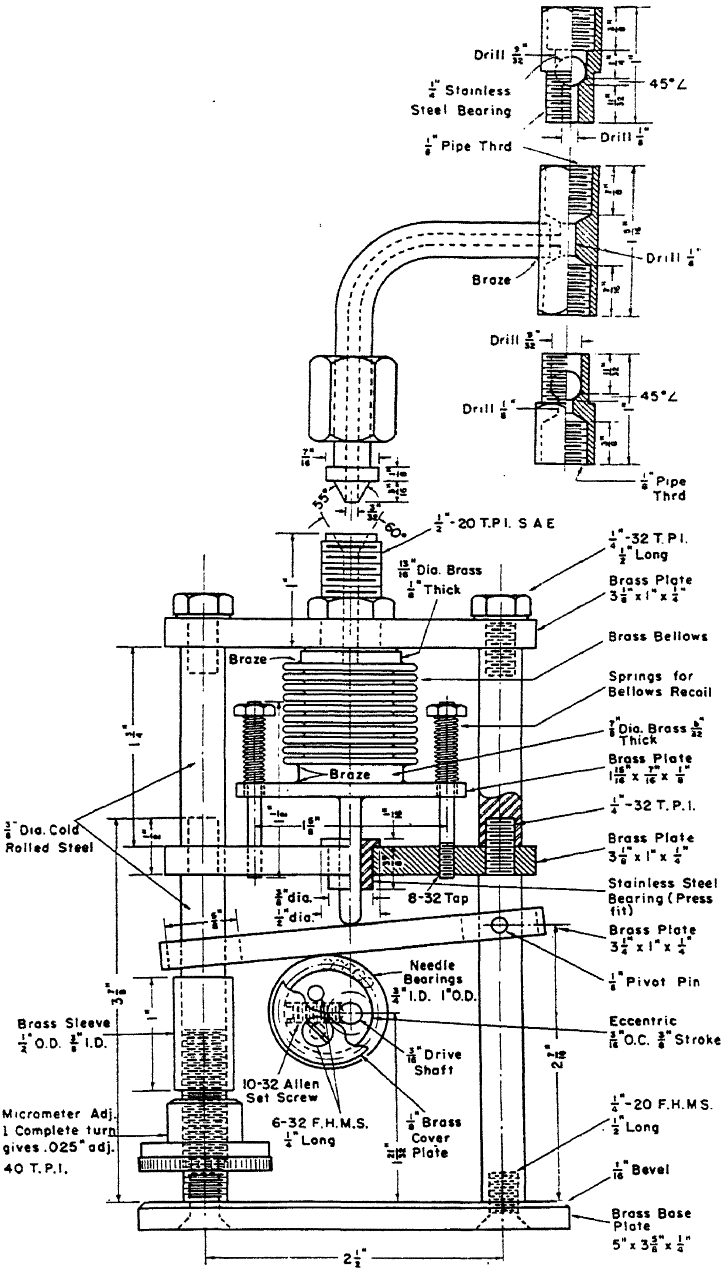
Drill 9/32"
1/4" Stainless Steel Bearing
45°∠
Drill 1/8"
1/8" Pipe Thrd
Braze
Drill 1/8"
Drill 3/32"
45°∠
Drill 1/8"
1/8" Pipe Thrd
7/16"
55°
3/32"
60°
1/2"-20 T.P.I. S A E
13/16" Dia. Brass 1/8" Thick
1/4"-32 T.P.I. 1/2" Long
Brass Plate 3 1/8" x 1" x 1/4"
Brass Bellows
Braze
Springs for Bellows Recoil
7/8" Dia. Brass 5/32" Thick
Braze
Brass Plate 1 15/16" x 7/16" x 1/8"
1 1/4"
1 5/8"
1/4"-32 T.P.I.
3/8" Dia. Cold Rolled Steel
Brass Plate 3 1/8" x 1" x 1/4"
3/8" dia.
1/2" dia.
8-32 Tap
Stainless Steel Bearing (Press fit)
5/8"
Brass Plate 3 1/4" x 1" x 1/4"
1/8" Pivot Pin
Needle Bearings 3/4" I.D. 1" O.D.
Eccentric 3/16" O.C. 3/8" Stroke
1"
Brass Sleeve 1/2" O.D. 3/8" I.D.
3/16" Drive Shaft
10-32 Allen Set Screw
6-32 F.H.M.S. 1/4" Long
1/8" Brass Cover Plate
Micrometer Adj. 1 Complete turn gives .025" adj. 40 T.P.I.
1/4"-20 F.H.M.S. 1/2" Long
1/16" Bevel
Brass Base Plate 5" x 3 3/8" x 1/4"
2 1/2"

Fig. 12. Bellows pump.[39]

Vaporization. A simple method of introducing liquids is by bubbling a gas through the liquid maintained at a temperature such that the vapor pressure of the liquid provides the desired ratio of gas to vaporized liquid[41] (Fig. 13). This method is especially applicable for catalytic reactions using one gaseous reactant, which serves to transport the vaporized liquid.

In the apparatus shown in Figure 13, hydrogen is used as a carrier gas to transport benzene vapors to a catalytic furnace. The hydrogen is purified by passage over copper gauze at 550°C., anhydrous calcium chloride, Ascarite, and Anhydrone. The mixture of hydrogen and benzene is obtained by bubbling the purified hydrogen through benzene contained in a spiral wash bottle. The ratio of hydrogen to benzene is controlled by the temperature of the benzene liquid.

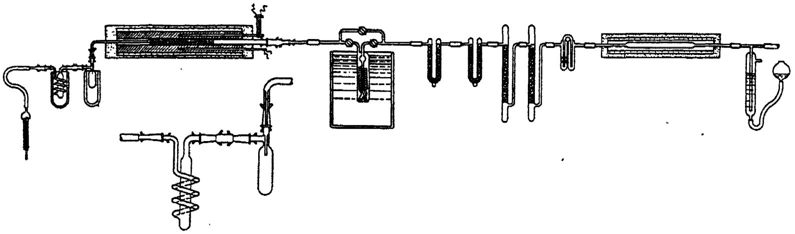

Fig. 13. Apparatus for hydrogenation of benzene.[41]

Hydrogenation takes place in the presence of the catalyst and the liquid catalysate is collected in receivers cooled in carbon dioxide – trichloroethylene. A catalyst prepared by reducing copper oxide (containing 0.1% nickel) for 20 hours at 225°C., yielded 47% cyclohexane at 90 seconds contact time and a temperature of 225°C.[41]

Introduction of Solids. Occasionally it becomes necessary to charge solid reactants into the catalyst system. If the vapor pressure of the solid is sufficiently high and a carrier gas can be employed, the method of liquid vaporization can be used, *i.e.*, the carrier gas passes through a molten layer of the solid.

If the solid can be melted at temperatures up to about 200°C. an adaptation of the variable capillary feeder to solids can be used (Fig. 14). A liquid is contained in the surrounding jacket *A* and sufficient heat is applied to the side arm *B* to melt the solid. To obtain a constant temperature, a liquid of appropriate boiling point should be used along with a condenser attached to *C*. The position of wire *D* relative to the capillary *E* permits the rate of feeding to be controlled. A slow stream of reactant or inert gas may be admitted at *F* to help the movement of melted solid material down into the reaction zone.

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[41] Ipatieff, Corson, and Kurbatov, *J. Phys. Chem.*, **43**, 593 (1939).

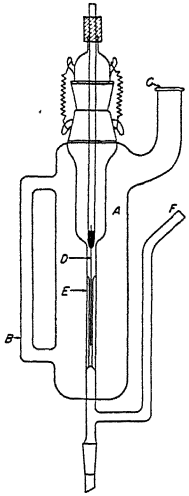

Fig. 14. Apparatus for feeding low melting point materials at constant flow.

Furnaces. For catalytic reactions at high temperature, it is necessary to provide a constant temperature reaction zone. For this purpose, a metal block furnace proved to be useful.[42] The furnace proper is illustrated in Figure 15 and consists of an aluminum bronze block (90% copper, 10% aluminum), suitably insulated and equipped with electrical resistance coil heaters. The aluminum bronze permits continuous use up to 700°C. and permits intermittent use up to 800°C. A constant temperature zone will be obtained except for about 16 cm. at top and bottom. In the furnace shown the diameter of the catalyst tube should be only slightly less than the diameter of the hole in the block. A tight seal between the tube and furnace should be made with asbestos string to avoid a chimney effect which would disrupt the temperature distribution.

This type of furnace is usually equipped with a special thermoregulator which is described in the section on temperature regulation.[43] If desired, this furnace can be used also in a horizontal or slightly inclined position.[44]

Resistance Furnace. A type of furnace for reactions requiring maintenance of a catalyst tube at an elevated temperature is comprised of coiled Chromel resistance wire wound around an Alundum core equipped with a spiral groove. It is a simple matter to construct such furnaces (see section on design of resistance heaters in the chapter on heating and cooling by Egly[45]). This design can be operated continuously up to 870°C. and intermittently up to 1000°C. However, assembled furnaces are relatively inexpensive and generally satisfactory.[46]

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[42] Thomas and Egloff, *Temperature, Its Measurement and Control in Science and Industry*. Reinhold, New York, 1941, pp. 617–623.

[43] The complete unit is available from *Precision Scientific Co.*, Chicago, Ill.

[44] See Figure 21, page 37.

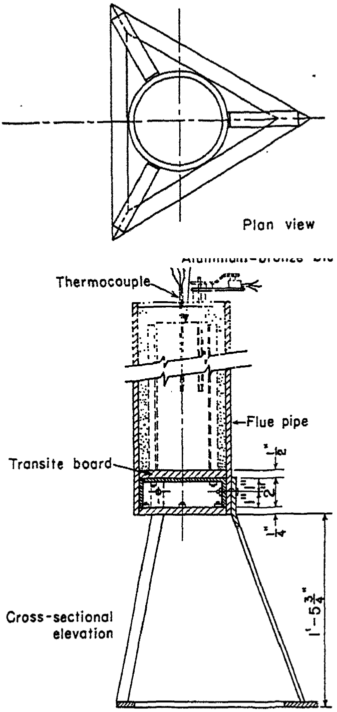

Fig. 15. High-temperature, aluminum–bronze block furnace.[42]

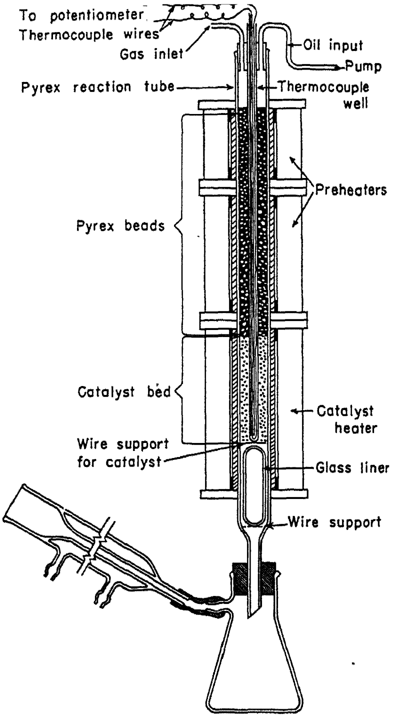

Fig. 16. Furnace for catalytic reactions.[46]

Wendland[47] has devised a reaction furnace from a three-section electrically heated combustion furnace of the Liebig type (Fig. 16). This apparatus was utilized for vaporizing a liquid on the Pyrex-bead preheater contained in the upper section of the catalyst tube.

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[45] Egly, "Heating and Cooling," this series.

[46] Furnaces of this design are available from *Hoskins Manufacturing Co.*, Detroit, Mich.

[47] Wendland, *J. Chem. Ed.*, 21, 171–174 (1944).

For still higher temperatures, combustion tube furnaces employing exposed resistance heating wire or bars may suitably be employed. Ordinarily, however, temperatures above 600°C. are not encountered in catalytic reactions although catalytic effects are noted at temperatures of 1000° and higher.

Heat-Transfer Baths. It is sometimes imperative to absorb a large amount of heat while maintaining a constant catalyst temperature. One of the best methods of achieving this is to surround the reaction tube with a liquid of high heat capacity maintained in rapid motion relative to the tube. Dependent upon the temperature range, various fluids can be employed as shown in Table I. Construction of heat-transfer baths and choice of bath media are discussed elsewhere.[45]

TABLE I

Important Heat Transfer Fluids

Fluid	Usual temperature limits, °C.	Usual pressure limits, atmospheres, gage
Steam or water	0 to 240	0–30
Oil	0 to 290	
Dowtherm A[a]	12 to 370	
Mercury	−38 to 540	0–12
HTS[b]	145 to 540	0
Lead	330 to 650	0

[a] 75% diphenyl oxide, 25% diphenyl.
[b] 40% $NaNO_2$, 7% $NaNO_3$, 53% KNO_3.

Of the available materials, HTS (*E. I. du Pont de Nemours & Co.*, Wilmington, Delaware and Dowtherm (*Dow Chemical Co.*, Midland, Michigan) have proved to be satisfactory in both industrial installations and laboratory installations as a means of controlling catalyst bed temperatures. To construct a furnace or reactor, it has been found convenient to pass a reaction tube vertically through a bath of electrically heated molten salts, or heat transfer liquids in a nitrate bath. A circulative pump or stirrer provides sufficient agitation to insure a uniform temperature. It is necessary to keep the bath covered to prevent the chance droppage of material which might cause an explosion (*e.g.*, carbonaceous material or water). It is also advisable to provide a return lip on the top of the bath since the hot liquid has a pronounced tendency to creep over the upper edge. Outside of these simple precautions, HTS is entirely satisfactory. With Dowtherm, the liquid must be maintained under pressure; control of the bath pressure affords a convenient method of temperature control.

Dielectric Heating. High-frequency dielectric heating has been successfully applied as a means of bringing solid catalyst to a desired reaction temperature.[48] Since the heating arises within the catalyst due to rotational motion of molecules or translational oscillation of ions, the catalyst is heated uniformly from inside and the ordinary factors of heat transfer are not involved. Naturally only solid catalysts which are dielectric in nature can be heated by the high-frequency electric field.[45]

A laboratory installation consists of a Pyrex tube filled with catalyst and two brass electrodes, clamped on both ends of the catalyst bed outside the glass tube, and connected to a radio frequency generator. The method appears to have particular application for endothermic reactions where heat must be supplied from external sources to maintain a reaction temperature.

Temperature Regulation. The temperature of certain catalytic reaction furnaces is readily controlled by means of standard temperature controllers. However, several expedients are available which are particularly adapted to laboratory use.

In the simplest method of control, the voltage supplied to the resistance heating elements is manually adjusted by means of a variable resistance or a variable transformer. The latter method should be preferred since losses are negligible whereas the variable resistance by its very nature wastes the electricity which is not actually used by the furnace elements. A variable transformer gives a continuously variable secondary voltage which is capable of fine adjustment. In either case, temperatures should be checked at frequent intervals since a fluctuating line voltage will change the voltage delivered to the heating element.

In the case of the aluminum bronze block furnace developed by Universal Oil Products Company, a unique type of differential expansion thermoregulator has been developed.[49] A porcelain rod is inserted in a hole drilled in the metal block. The difference in thermal expansion of the porcelain rod and the metal block is magnified by a

[48] Komarewsky, *Science*, **105**, 291 (1947).

[49] Thomas and Egloff, *loc. cit.*, pp. 617–623.

lever arm to electrical contact points (Fig. 17). To raise the temperature the set screw is turned in to make electrical contact through the points, which in turn actuates a relay and causes electricity to flow to the furnace heaters. To set the temperature the screw is set by trial and error to give the desired temperature. When shutting down the furnace, the set screw must be unscrewed to avoid damage to either the porcelain rod or the control mechanism. While the device

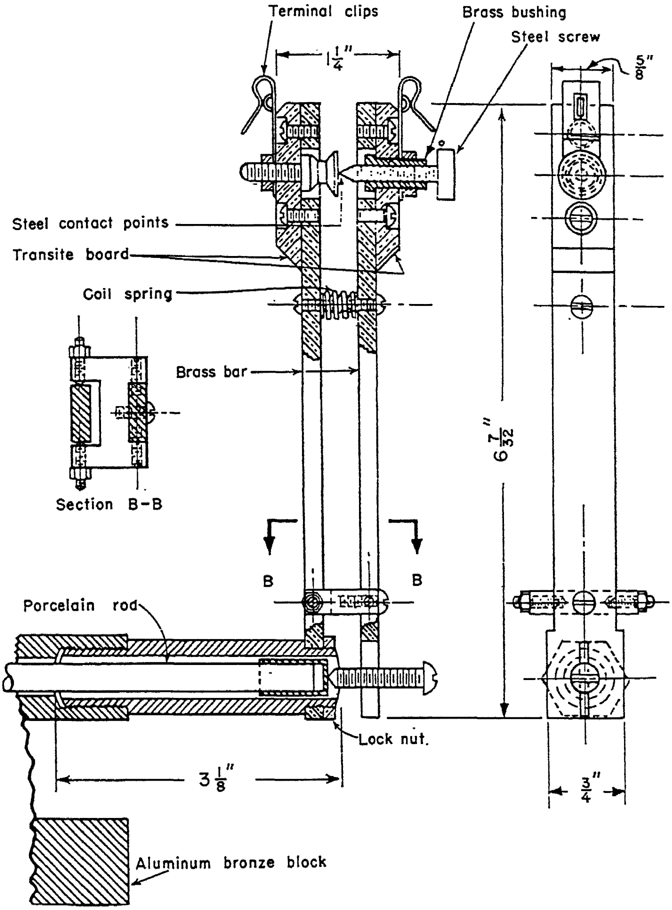

Fig. 17. Differential expansion thermoregulator for block furnace.[49]

is fully automatic, it is a wise precaution to check the temperature occasionally to avoid overheating in case of a sticking contact point. If exposed electrical contacts are objectionable, a fully enclosed microswitch[50] as shown in Figure 18 may be employed instead of the open contact points.

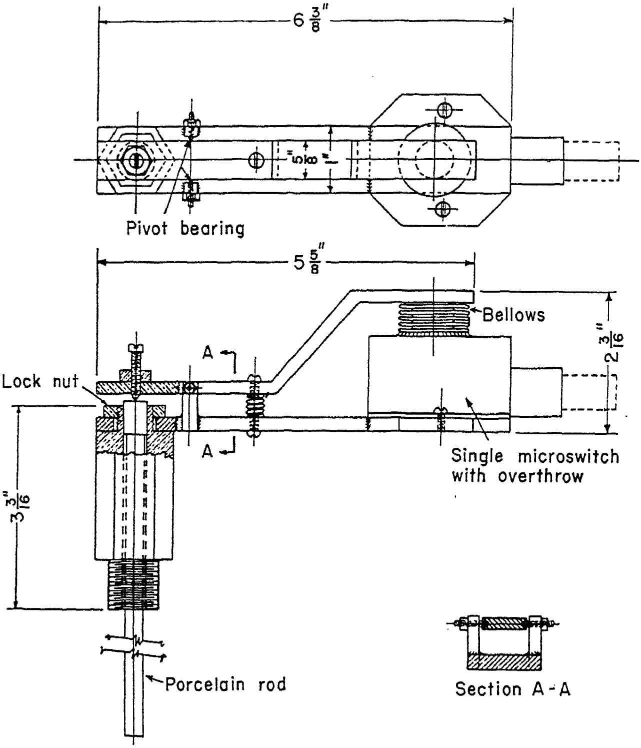

Fig. 18. Temperature controller with enclosed microswitch.[49]

In addition to the above devices any of the automatic temperature controlling, indicating, or recording instruments may be used to control the temperature of the furnace.[45,50a]

Catalytic Reactors. At atmospheric pressure it is convenient to use reactors constructed of Pyrex glass for temperatures up to about

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[50] Micro Switch Co., Chicago, Ill.

[50a] Sturtevant, in *Physical Methods of Organic Chemistry.* 2nd ed., Chapters I and II, Interscience, New York.

530°C. For higher temperatures quartz may be employed. Both are well suited for reactors because of their relatively low catalytic effect, ease of fabrication, and the possibility of visual inspection of the catalyst bed. Various forms of catalyst tubes are possible but the designs shown in Figure 19 are simple and effective. The granulated catalyst is suitably held in place by means of a small plug of Pyrex glass wool (below 530°C.). The catalyst tubes *B* and *C* illustrate means of conducting liquids or vapors past ground-glass joints.

If metal reactor walls are employed, the simple tube is probably the most useful form. Variations involving coiled tubing, finned interiors, and annular spaces are applicable to reactions which are strongly exothermic or endothermic.

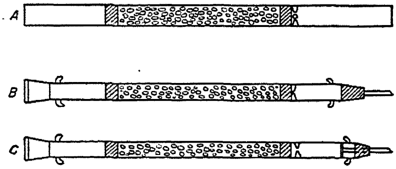

Fig. 19. Simple forms of glass catalytic tubes.

One of the most effective methods of providing contact between gaseous reactants and a solid catalyst is based on the fluidized solids principle. The catalyst in the form of a powder is fluffed into a condition resembling a liquid by upward passage of gases or vapors at a rate of 15–45 cm. per second superficial linear velocity (*i.e.*, the linear velocity which would prevail in the absence of the catalyst powder). A suitable reactor for studying fluidized catalyst reactions[51] is shown in Figure 20. The gases enter through a small piece of 100-mesh screen placed at the bottom of the cone. Catalyst temperature as measured by means of the thermocouple will be quite uniform throughout the depth of the bed due to the violent agitation of the moving catalyst particles. Another fluidized catalyst, designed to have a length-to-diameter ratio of 18, has been developed for rating the activity of powdered catalytic cracking catalysts.[52]

The pressure drop attending the flow of gases upward through a fluidized bed of solids is equivalent to the suspension head regardless of the nature of the gas or the solids or the flow rate.[53]

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[51] Thomas and Hoekstra, *Ind. Eng. Chem.*, **37**, 332–334 (1945).

[52] McReynolds, paper presented before the American Petroleum Institute, November 10, 1947, Chicago, Ill.

[53] Parent, Yagol, and Steiner, *Chem. Eng. Progress*, **43**, 429–436 (1947).

Despite the advantages of fluidization for effecting intimate contact between solid catalyst and gaseous reactants, there are several disadvantages for generalized laboratory application: (*1*) the velocity range to obtain fluidization is relatively narrow and does not permit a great deal of flexibility; (*2*) problems in dust entrainement and separation may arise through the use of the technique; and (*3*) the process requires extensive automatic controls if a continuous catalyst regeneration is made to maintain a constant catalytic activity. In general the technique is not readily adapted to ordinary laboratory studies but can be used to advantage in a pilot plant[54] or for small-scale production.

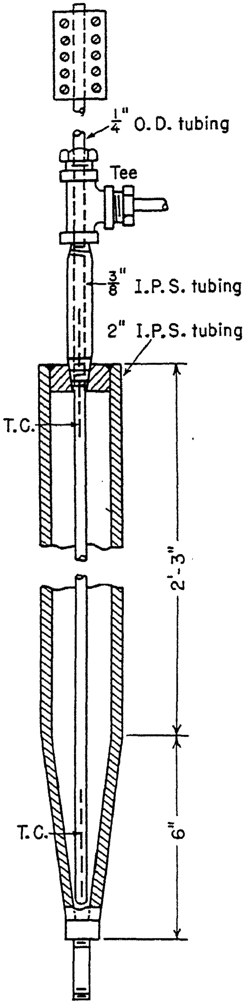

Fig. 20. Fixed bed fluidizing unit.[51]

Collection of Products. The collection of products is usually done by condensation at temperatures convenient in the laboratory, namely, cooling water, ice, salt–ice mixture, Dry Ice, and liquid nitrogen. Suitable apparatus for condensing a liquid is shown[55] in Figure 21. It consists of a water cooler and an ice condensation unit. A sample of gas is withdrawn by a special gas sampling bottle. This device requires no pressure for operation, is simple in construction, and permits measurement of a sample by displacement of salt water. Final measurement of gases not condensed is done by means of a wet test meter. Figure 22 illustrates the use of several condensers and traps in series to condense the reaction products more effectively.[55]

[54] Anon., *Oil Gas J.*, 45, No. 43, 82–83 (1947).

[55] Komarewsky and Riesz, *Oil Gas J.*, 42, No. 7, 90–93, 119 (1943).

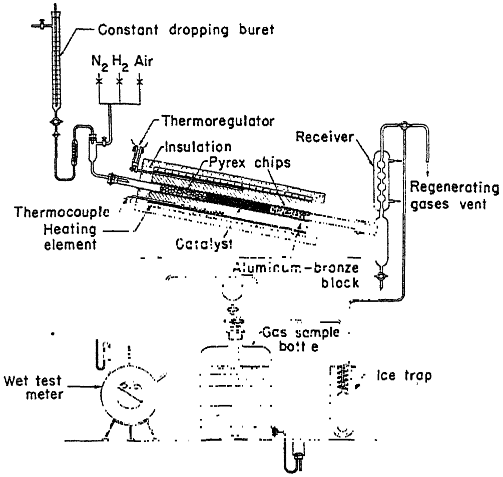

Fig. 21. Atmospheric flow apparatus with inclined block furnace.

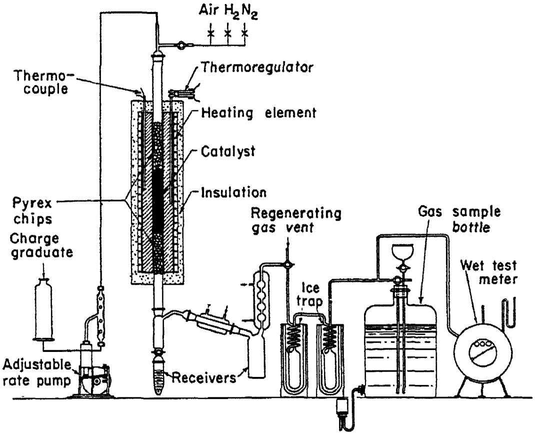

Fig. 22. Atmospheric flow apparatus with vertical furnace.

2. Catalytic Reactions at Subatmospheric Pressure

Many catalytic reactions can be advantageously carried out *in vacuo*. For example, reactions of the type:

$$A \rightarrow B + C$$

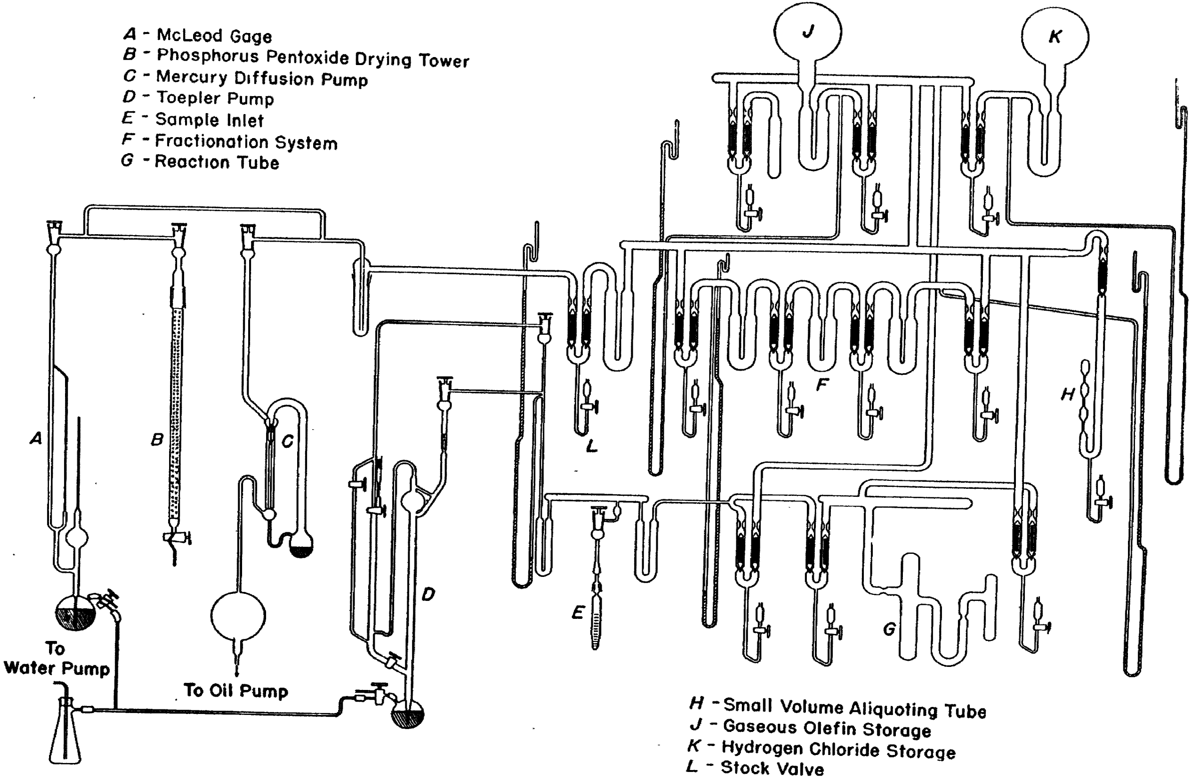
A - McLeod Gage
B - Phosphorus Pentoxide Drying Tower
C - Mercury Diffusion Pump
D - Toepler Pump
E - Sample Inlet
F - Fractionation System
G - Reaction Tube
J
K
A
B
C
L
F
H
D
E
G
To Water Pump
To Oil Pump
H - Small Volume Aliquoting Tube
J - Gaseous Olefin Storage
K - Hydrogen Chloride Storage
L - Stock Valve

Fig. 23. High-vacuum apparatus for studying isomerization.

will proceed more rapidly at reduced pressures according to the Le Chatelier principle. Alternately, it may be necessary to conduct the reaction at low pressure in order to obtain reactants or products in the vapor phase. The following section describes techniques for conducting catalytic reactions at subatmospheric pressure.

A. BATCH SYSTEMS

The use of standard high-vacuum techniques can be applied to batch catalytic reactions with but slight modifications occasioned by the particular catalyst employed. A specific example of the batch subatmospheric pressure system is that of Pines and Wackher.[56] The apparatus is illustrated in Figure 23. Special provision has been made so that the catalyst is never contaminated with any undesirable material. To eliminate extraneous effects catalyst and reactants come in contact only with glass or mercury.

The apparatus shown in Figure 23 has been used to study the isomerization of normal butane in the presence of aluminum chloride – hydrogen chloride catalyst.[56] The aluminum chloride was purified by melting at 180–190°C. under 100 atmospheres of hydrogen pressure in a glass liner contained in a steel bomb; aluminum chloride crystals sublimed to the top of the liner upon cooling. These crystals were powdered and stored in airtight containers. Hydrogen chloride was prepared by the reaction of sulfuric acid and sodium chloride followed by passage through Dry Ice – acetone traps and phosphorus pentoxide to remove the last traces of water.

Normal butane (7.2 g.) was isomerized in the presence of 1.5 g. aluminum chloride and 0.27 g. hydrogen chloride at a temperature of $-100°C$. With a reaction time of 12 hours, 27% of isobutane was produced, provided that the butane contained 0.28% butenes.

A generalized treatment of vacuum techniques may be found in the book of Farkas and Melville.[57]

B. FLOW SYSTEMS

The vapor pressure of the reactant can conveniently serve to produce a constant flow of vapors; this is illustrated in Figure 24, where the reactant in vessel *F* was heated and the vapors passed over the catalyst in *K* which was maintained in a bath of molten potassium and sodium nitrates.[58]

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[56] Pines and Wackher, *J. Am. Chem. Soc.*, 68, 595–605 (1946).

[57] Farkas and Melville, *Experimental Methods in Gas Reactions*. Macmillan, London, 1939.

[58] Hoover and Rideal, *J. Am. Chem. Soc.*, 49, 111 (1927).

The arrangement shown in Figure 25 has been devised[59] to permit the collection of gases produced during the course of the reaction. The liquid reactant is pumped into the system by means of a bellows pump. Following the catalytic reaction, condensable products are collected in ice and Dry Ice traps. Formation of noncondensable gas causes the system pressure to rise and closes an electrical circuit in the automatic pressure regulator; this, in turn, actuates the vacuum pump through a relay until the system pressure has been reduced to the set value. A similar arrangement has been employed for use with a gaseous reactant.[60]

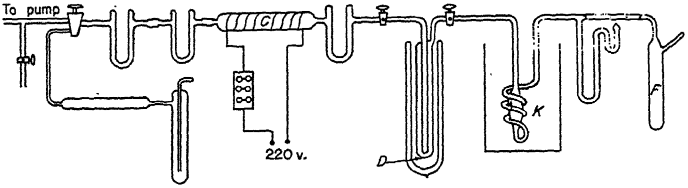

Fig. 24. Arrangement for low-pressure catalytic reaction.[58] (*D* is trap which may be immersed in liquid air.)

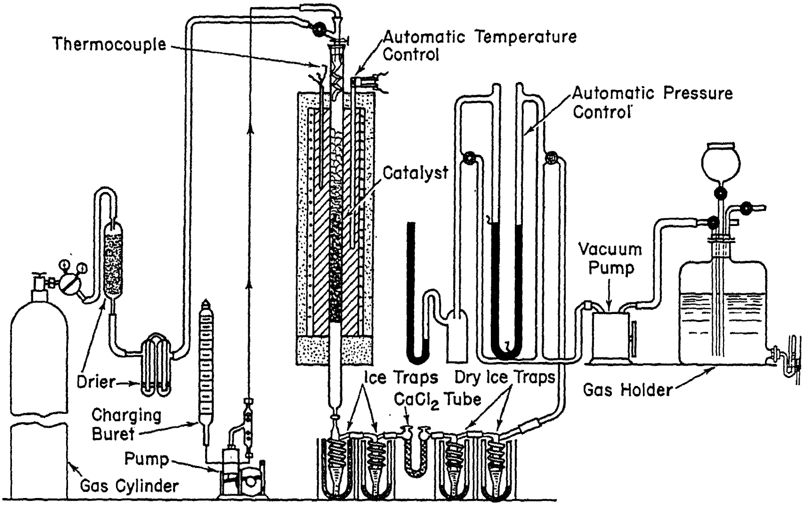

Fig. 25. Apparatus for conducting catalytic reaction at reduced pressure.[59]

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[59] Komarewsky and Stringer, *J. Am. Chem. Soc.*, **63**, 921 (1941).

[60] Komarewsky and Riesz, *Oil and Gas J.*, **41**, No. 19, 33, 37, 39 (1942).

In the apparatus, shown in Figure 25, isoamyl alcohol was dehydrated and dehydrogenated to isoprene using a mixed complex-action catalyst. Chromia-alumina (4% Cr_2O_3, 96% Al_2O_3) catalyst was prepared by the impregnation of activated alumina with the calculated amount of chromium nitrate. The catalyst was dried and reduced in hydrogen at 600°C. At 600°C., 130 mm. absolute pressure, and 0.34 liquid space velocity per hour, 16% isoprene was formed.[59]

To illustrate use of a gaseous reactant, normal butane was dehydrogenated to butenes and butadiene over the same chromia-alumina catalyst. At a temperature of 650°C., absolute pressure of 95 mm., and a gaseous space velocity of 220 per hour, 20% by weight butenes and 13% butadiene was formed.[60]

3. Catalytic Reactions at Superatmospheric Pressure

High pressures have found wide application in the field of catalysis. Reactions that do not occur or proceed slowly at atmospheric pressure can be catalyzed at high pressure to obtain the desired result in a short time. Ammonia synthesis, methanol production, and coal hydrogenation are examples. Along with such industrial developments, high-pressure techniques in laboratory applications have been improved simultaneously and continuously. The following discussion will give some understanding of the basic principles of high-pressure technology and demonstrates techniques of applying superatmospheric pressure to catalytic reactions on a laboratory scale. Both batch and continuous flow apparatus are considered.

A. CALCULATION OF REACTOR DIMENSIONS

By far the most important problem in high-pressure technology is the design of the reactor for conducting the catalytic reaction. This is, indeed, a matter for the specialist since an error could have serious consequences. However, the chemist should have an understanding of the basic principles of design to assist in evaluating the problems of high-pressure techniques.

It is basic that within its tensile and compressive elastic limits, a material can be stressed without deformation. Above the elastic limits, permanent deformation or even rupture may occur as a result of applied stresses. The cause of elastic failure is not known and the mathematical theory of elasticity is confined to those limits within which Hooke's law is obeyed, *i.e.*, within the elastic limits of any body, the ratio of the stress to the strain produced is constant.

Most high-pressure equipment is cylindrical in form and, ordinarily, the problem can be resolved to the calculation of internal and external radius for a given internal pressure. When an internal pressure is exerted against a cylinder wall, the principal stresses are a compressive radial stress, a tensile hoop stress, and a longitudinal stress. The assumption is made that when the stresses in any part of the system exceed the elastic limit, it has begun to fail.

This is not entirely valid since it is generally recognized that the tensile stresses in a thick cylinder increase more rapidly on the inside than on the outside of the cylinder. When the inner layers are stressed to the yield point, plastic flow can occur and redistribute the stresses in the outer layer without failure by a process known as autofrettage. However, the assumption that failure at any part of the system implies potential failure of the entire structure is useful in practice and four methods of calculating the pressure at which the stresses in the inner surface reach the yield point are identified according to the theory from which they are derived.[61]

Let P = internal radial pressure acting on the inner wall of the cylinder, kg./sq.cm., S = stress equal to elastic limit, kg./sq.cm., R_i = inner radius, cm., and R_o = outer radius, cm. Then:

(*1*) The *maximum principal stress theory* shows that the internal pressure will cause the stresses at the inner wall to coincide with the elastic limit under simple tension when:

$$P = \frac{R_i^2 - R_o^2}{R_i^2 + R_o^2} S$$

(*2*) From the *maximum strain theory* elastic failure will occur when the maximum strain equals the strain at the elastic limit under simple tension and, if the coefficient of lateral contraction, or Poisson's ratio, is 0.25, the relationship becomes:

$$P = \frac{4(R_i^2 - R_o^2)}{5R_i^2 + 3R_o^2} S$$

(*3*) If elastic failure occurs when the *maximum shear stress* reaches a critical value, the equation is:

$$P = \frac{R_i^2 - R_o^2}{2R_i^2} S$$

(*4*) According to *strain energy theory*, the strain energy per unit volume reaches a critical value when:

$$P = \frac{2(R_i^2 - R_o^2)}{(10R_i^4 + 6R_o^4)^{1/2}} S$$

For reactor design it is possible to use the above theories, the working or allowable stress being the yield point divided by a suitable factor of safety, usually higher than two. Newitt[61] presents data showing that with brittle materials such as cast iron, the maximum principal stress theory applies, whereas for ductile materials, the maximum shear stress and the strain energy theory holds more closely. For high tensile steels, the data of Macrae demonstrate that the maximum shear stress theory gives the closest approach to experimental results; it is recommended for calculations involving these steels.

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[61] Newitt, *The Design of High Pressure Plant and Properties of Fluids at High Pressures*. Clarendon Press, Oxford, 1940.

For completeness of presentation the practical methods used for pressure design should be mentioned. For pressures below 170–200 atmospheres the A.S.M.E. Code for Unfired Pressure Vessels[62] can be used. If one considers the vessel as a thin-walled cylinder:

$$P = St/R$$

where t is the wall thickness in centimeters. The formula given in the code specifies:

$$P = St(R_i + 0.6t)$$

The formula used in the A.P.I.–A.S.M.E. Code[63] is quite similar:

$$P = \frac{(t - c)}{R_m} S$$

where R_m = mean radius, in centimeters, before corrosion allowance and C = allowance for corrosion, in centimers.

These formulas are intended to apply below 170–200 atmospheres; for higher pressures, one of the thick-wall formulas, such as that based on maximum shear stress, should be employed.

The question of *temperature* has not been considered thus far but it is of the utmost importance because a large number of catalytic reactions also require high temperatures as well as pressures. When heat is transferred through the walls of the pressure vessel, the stress distribution is changed. For example, if heat is supplied from the outside, the outer fibers are kept from expanding freely by the rigidity of the inner structure of the cylinder so that the outer fibers are under compression while the inner ones are under tension. In this case the cylinder is weakened so that thicker walls would be needed to counterbalance this effect plus that due to the internal pressure. With a temperature gradient due to internal heating, the tensile stresses in the inner layers of the cylinder walls are reduced so that the cylinder is strengthened relative to the condition where there is no temperature gradient.

B. METHODS OF REACTOR CONSTRUCTION

In a simple, thick-wall cylinder, the stress distribution due to internal pressure is not uniform through the walls but is much greater at the inner wall. In the case where the outer radius is twice the inner radius, it is estimated that the stress on the outside surface of the vessel is only 40% as great as that of the inside surface.[64] For a proper distribution of such working stresses in thick-wall cylinders, three methods are available: (*a*) by forming a compound cylinder, (*b*) by multilayer or wound construction, and (*c*) by autofrettage. A compound cylinder is formed by heating a machined outer tube until it will fit over an inner tube, machined to a calculated external diameter. Upon cooling this duplex cylinder the contraction of the outer tube is resisted by the compressive elasticity of the inner one and, provided that the heating has been uniform and the contacting surfaces have been accurately machined, radial stresses are developed. The inner tube is thus under compression so that upon applying an internal pressure, the resultant hoop stresses will be less in the inner tube. Consequently, a more uniform distribution of stresses is attained than would be found in a similar simple thick-walled cylinder. By use of three or more relatively thin cylinders in a compound cylinder, still better stress distribution is possible.

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[62] *Rules for the Construction of Unfired Pressure Vessels, Section VIII, A.S.M.E. Boiler Construction Code.* American Society of Mechanical Engineers, New York, 1943.

[63] *A.P.I. - A.S.M.E. Code for the Design, Construction, Inspection, and Repair of Unfired Pressure Vessels for Petroleum Liquids and Gases.* American Petroleum Institute, American Society of Mechanical Engineers, New York, 1946.

In multilayer or wound fabrication, compressive stresses are produced in an inner tube by winding it with steel wire or ribbon at high tension. This method is particularly useful in constructing industrial reactors. The innermost layer can be made of corrosion-resistant material while the reinforcing layers can be made of the most economical material for resistance to temperature and stresses set up by the internal pressure. It should be noted that temperatures above 370–425°C. stress relieve the wrappings and nullify the improvement. To make effective use of the steel, it has been estimated that when the ratio, $R_o/(R_o - R_i)$, becomes 2.5 or less, a modification of the simple cylinder construction is justified.[64]

Autofrettage is a third method of fabricating thick-walled vessels to distribute more uniformly the working stresses caused by internal pressure. The procedure consists in applying an internal pressure to obtain a controlled overstressing of the inner layers of the cylinder beyond the elastic limit. When the pressure is released the fibers of the inside surface of the cylinder remain in compression and those of the outside in tension. This method cannot be employed in vessels which may be subjected to temperatures sufficient to relieve the stresses which were purposely imposed upon the metal walls.

[64] Jasper and Scudder, *Trans. Am. Inst. Chem. Engrs.*, **37**, 885–905 (1941).

C. MATERIALS OF CONSTRUCTION FOR HIGH-PRESSURE REACTORS

It is difficult to give generalized rules for the selection of the materials of the wall of the reactor. For noncorrosive conditions at elevated temperatures, some of the recommended steels specified in the A.S.M.E. Code for Unfired Pressure Vessels can be applied.[65]

An evaluation of the suitability of stainless steel for high-temperature service can be made from the creep strength data presented in Table II.[66] It is customary to base design upon a creep rate of 0.01% per 1000 hours, permitting a maximum design stress at 816° C. of 102 kg./sq. cm. for this stainless steel (Table II).

TABLE II

Creep and Rupture Strength of 18-8 Stainless Steel (Timken)

Temperature, °C.	Stress (kg./sq. cm.) for designated creep rate[a]		Stress (kg./sq. cm.) for rupture in 100,000 hrs.	Ratio of creep strength (0.01%) to rupture strength
	0.01	0.10		
538	756	1265	—	—
593	559	928	—	—
649	302	577	506	0.60
704	176	387	260	0.68
760	127	281	183	0.69
816	102	200	120	0.85
871	—	—	84	—
982	—	—	39	—

[a] Rate in per cent per 1000 hours.

TABLE III

Analysis of High-Temperature Alloy S-816

Carbon	0.40	Cobalt	44.00
Manganese	1.50 (max.)	Molybdenum	4.00
Silicon	1.00 (max.)	Tungsten	4.00
Chromium	20.00	Columbium	4.00
Nickel	20.00	Iron	4.00 (max.)

For extremely high temperatures a special alloy known as S-816 has been developed for gas turbines and jet propulsion.[67] The nominal analysis of this alloy is given in Table III.

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[65] *Materials Specifications, Section II, A.S.M.E. Boiler Construction Code.* American Society of Mechanical Engineers, New York, 1943.

[66] *Digest of Steels for High Temperature Service.* 5th ed., The Timken Roller Bearing Co., Canton, Ohio, 1946.

[67] Wilson, *Materials & Methods*, **24**, 885–890 (1946).

Stress rupture curves for this alloy are given in Figure 26 and may serve as a basis for design of pressure vessels for high-temperature, high-pressure applications.

D. CLOSURES

The usual shape of a high-pressure vessel is cylindrical, one end being permanently closed while the other has a removable closure for cleaning the interior. Ordinarily, all entry, exit, and auxiliary connections are made through the removable head. If possible, entries into the sides of the vessel should be avoided.

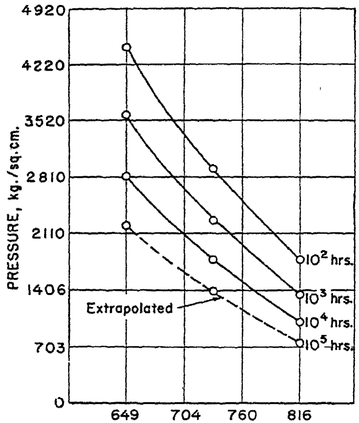

Fig. 26. Stress rupture curves of heat-treated alloy S-816.[67]

Small vessels (up to 15–20 cm. internal diameter) are commonly made by boring an appropriate piece of bar stock to form the pressure vessel. The closure in this case consists of the unbored end, the thinnest section being commensurate with the wall thickness of the cylindrical part (Fig. 27A). Square, sharp corners may be left in the vessel for pressures below 3500 atm. for simplicity of fabrication; above this value, it is safer to round the inside surface to eliminate stress concentrations at corners.

A second form of permanent closure is the solid forged end and this type is employed for internal diameters ranging from 15 cm. to 2 meters (Fig. 28B). The main difficulty with this method of forming a pressure vessel is that the equipment for making the hollow forging may be costly.

For service at 70 to 135 atm. pressure, a flat disk welded to the end of a cylinder is satisfactory (Fig. 27C). Above this pressure and above 15 cm. inside diameter, a butt-welded cap can be utilized up to about 1000 atm. (Fig. 27D).

The use of welding caps, welded screw plugs, cast steel, and various other methods of forming a closed end, as well as cost data for various other closure types, is discussed by Meigs.[68]

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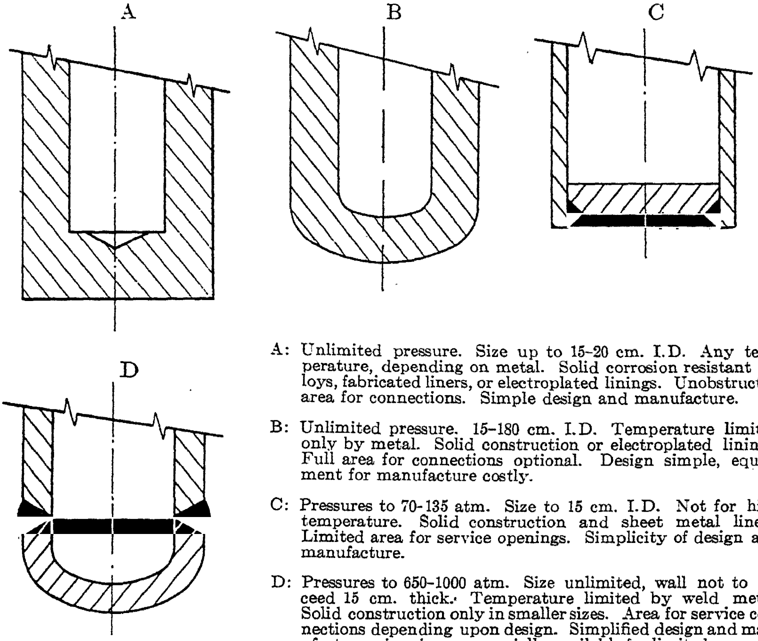
[68] Meigs, *Trans. Am. Inst. Chem. Engrs.*, **39**, 769–791 (1943).

Removable closures are necessary in all experimental high-pressure apparatus. Usually all connections are most satisfactorily located in a removable pressure head. The internal pressure against a closure surface must be counteracted by some mechanical device. For this purpose, bolts, screwed threads, or metal collars are ordinarily used and must be designed to withstand the maximum working pressure with an appropriate factor of safety. To obtain a gastight seal, a packing material is compressed so that the path of escaping material is blocked by a plastic layer or film of packing.



A: Unlimited pressure. Size up to 15–20 cm. I.D. Any temperature, depending on metal. Solid corrosion resistant alloys, fabricated liners, or electroplated linings. Unobstructed area for connections. Simple design and manufacture.

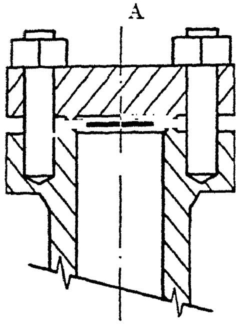
B: Unlimited pressure. 15–180 cm. I.D. Temperature limited only by metal. Solid construction or electroplated linings. Full area for connections optional. Design simple, equipment for manufacture costly.

C: Pressures to 70-135 atm. Size to 15 cm. I.D. Not for high temperature. Solid construction and sheet metal liners. Limited area for service openings. Simplicity of design and manufacture.

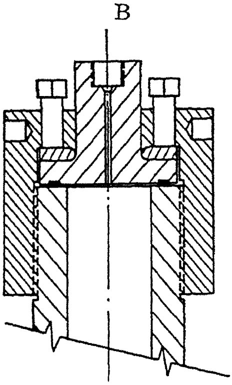
D: Pressures to 650-1000 atm. Size unlimited, wall not to exceed 15 cm. thick. Temperature limited by weld metal. Solid construction only in smaller sizes. Area for service connections depending upon design. Simplified design and manufacture; pipe size commercially available for limited pressure.

Fig. 27. Permanent closures.[68] A, solid bored end; B, solid forged end; C, flat disk welded; D, butt-welded cap.

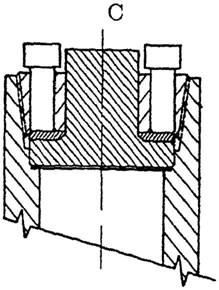
For pressures up to 270 atm., bolted flanges for screwing or welding to cylindrical sections are available from commercial sources. These function by squeezing a section of packing with a total bolt pressure greater than the internal pressure exerted against the closure internal surface. A fundamental principle in such designs is that there should be a high intensity of contact pressure produced by a relatively small coupling force.



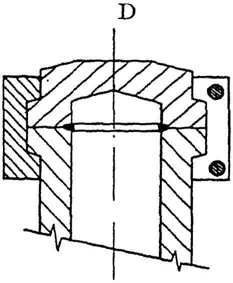
Slow opening closure—never sticks—easy to clean. Frequent gasket removal. Pressures to 400 atm. Sizes to 15 cm. I. D. O.K. for high temperature service. Solid metal construction only. Usually smaller than other types of flanges for same size. Design and manufacture costly. Forgings to order—careful lathe work.



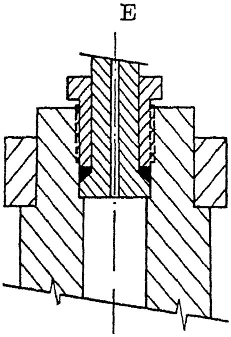
Quick-opening closure. Easy to clean. Pressures to 6700 atm., if using self-sealing gasket. Sizes from 2.5–15 cm. I. D. Temperature service limited by cap screw material. Adaptable to any type of corrosion-proof construction. Area limited for connections. Design and manufacture more critical than making flanges.



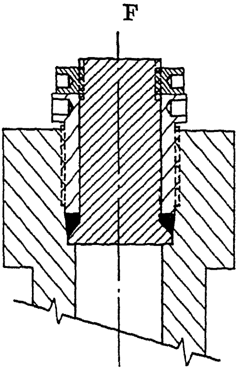
Quick-opening closure. Light weight. Not easy to clean. Pressures to 3400 atm., if using self-sealing gasket. Sizes from 15–40 cm. I. D. High temperatures limited by bolt stress. No metal wasted, important in solid alloy construction. Sheet metal linings O.K. Limited area for connections. Design critical. Manufacture less so.



Quick-opening closure. Light weight. Pressures up to 1700 atm. For large openings, over 30 cm. I.D. Advantageous for high temperatures, using self-sealing gasket. Economical of solid alloy metals—linings also practicable. Full area for end connections. Design and manufacture critical—machining difficult.



Not easy to open. For high pressures, 1700 atm. and up. Very small sizes, up to 5 cm. I.D. Temperature limited only by previous heat treatment of steel. Can-type liners for corrosion resistance. Requires precision in manufacture. Shrunk ring common.



Quick-opening for frequent removal—not easy to clean—low upkeep. Unlimited pressure range—self-sealing. Sizes 7.5–45 cm. I.D. Temperature limited only by metals. Can-type liners or solid construction for corrosion resistance. Ends are restricted—high radial stresses. Manufacture very difficult. High-precision work.

Fig. 28. Removable closures.[68] A, Ipatieff; B, Aminco; C, tapered cap ring; D, Vickers-Anderson; E, Bridgman; F, modified Bridgman.

It has been stated that if the pressure exerted upon the area of jointing faces is greater than the pressure to be resisted, the joint will function satisfactorily.[69] With the customary circular ring of contact, the minimum force, F, needed to retain tightness is then:

$$F = \frac{\pi}{4}(d + 2w)^2 P$$

where P = internal pressure, kg./sq. cm., d = internal diameter of ring, cm., and w = mean width of ring of contact, cm. Both d and w should be kept small to minimize the force necessary to maintain the seal. While d is fixed by the joint dimensions required, the width w is determined by practical considerations of the application. By the use of knife edges, the ring width becomes extremely small.

An inexpensive type of closure for small pressure vessels consists of a screwed plug bearing upon a fully confined gasket. Up to 5 cm. diameter, this closure is applicable to 3500 atm. The limitations of this closure include need for precise machining, requirement for large wrenches, and the smallness of the usable head area.

A type of closure much recommended for research apparatus is the Ipatieff closure (Fig. 28A). The seal is provided by circular knife edges which squeeze into a thick flat ring of soft-annealed copper. The closure is easy to open and clean and the device is very convenient if liquids need to be poured out of the vessel. Maximum pressure is about 400 atm; the limitation is the tensile strength of the bolts.

A factor contributing greatly to the bulkiness of flanged joints is that ordinarily the tensile stresses are carried by bolts which themselves are in tension. This is eliminated in the American Instrument Company joint and in the Vickers-Anderson type of joint. In the Aminco closure (Fig. 28B), a ring of small cap screws in compression provides the sealing force and uniform pressure can be applied to the shoulder of the bolt. It is recommended that a torsion meter be utilized to provide uniform application of a tightening wrench. The Aminco closure is well suited for laboratory reactors of 2 to 13 cm. inside diameter. For larger openings, up to 40 cm. inside diameter, a tapered cap-ring closure (Fig. 28C) is recommended by Meigs.[70] This type is quick-opening and requires relatively less metal than other wide-mouth closures now in use.

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[69] Newitt, *The Design of High Pressure Plant and Properties of Fluids at High Pressures*. Clarendon Press, Oxford, 1940, p. 78.

[70] Meigs, *Trans. Am. Inst. Chem. Engrs.*, **39**, 786–787 (1943).

In the Vickers-Anderson type of closure (Fig. 28D) all tensile stresses across the closure are carried by a closely fitting collar, made in several segments and pulled up by tangential bolts. The sealing faces of the joint are forced together by the slight angle of the shoulder faces. This closure is particularly useful for pressures over 135 atm. and diameters over 60–90 cm.; maximum pressure can be as high as 1700 atm.

In recent years closures using Bridgman's principle of the unsupported area[71] have come into wide application particularly for the economical use of metal in large, high-pressure vessels. An unsupported area in some form is the basis for all self-sealing closures including conical gaskets, lens rings, and hollow rings. The Bridgman closure in its simplest form is shown in Figure 28E. The tendency to force out the entering tube is transmitted to the screwed sleeve through the packing. The force due to internal pressure is exerted over the entire area of the face of the plug. The total force exerted through the packing must be equal and opposite, but this force is applied only to the annular area. Consequently, the pressure exerted on the packing is higher than the internal pressure in direct proportion to the ratio of these two areas and the pressure applied to seal the packing is automatically maintained at a fixed percentage above the internal pressure. The design shown can be used for pressures of 1700 atm. and higher but is limited to small sizes (5 cm. or less).

A more convenient form of closure is shown in Figure 28F, in which a hardened and polished steel ring is used in place of a soft gasket, its seat being tapered to eliminate sticking. This design is suitable for 7–45 cm. diameter openings; it is quick-opening and properly proportioned, and is well adapted for pressures of 200–1700 atm. or higher.[72]

An adaptation of the self-sealing closure was employed in the Bureau of Mines design of an autoclave for the hydrogenation of coal.[73] The details of the assembly are shown in Figure 29. The seal is obtained by means of a copper sealing ring, *A*, supported by a

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[71] Bridgman, *The Physics of High Pressures.* Macmillan, New York, 1931.

[72] Meigs, *Trans. Am. Inst. Chem. Engrs.*, **39**, 788–789 (1943).

[73] Fisher, Sprunk, Eisner, O'Donnel, Clarke, and Storch, *U. S. Bur. Mines Tech. Papers*, **642** (1942).

segmented stainless-steel retaining ring, *C*. The actual gastight seal is obtained by line contact of the inner surface of the carefully machined copper ring with the surface on the head machined to a slightly less acute angle. This seal has been satisfactory for service at 350 atm. and 460°C.

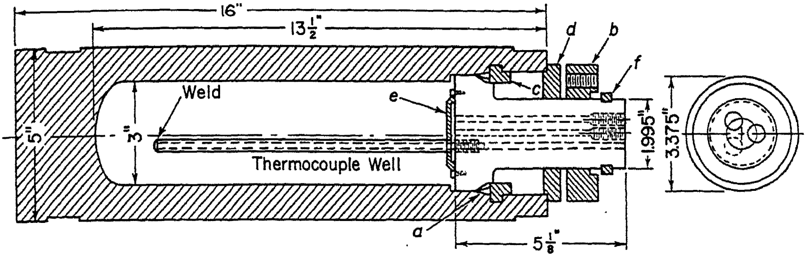

Fig. 29. U. S. Bureau of Mines autoclave: *a*, copper sealing ring; *b*, clamping ring; *c*, segmented retaining ring; *d*, centering ring; *e*, liquid seal plate; *f*, two-segment lifting ring.[73]

E. CONTROL AND MEASUREMENT OF HIGH PRESSURES

(1) Valves. For general purposes the main requirements for a high-pressure valve are: (*1*) ease of operation, (*2*) fine adjustment, and (*3*) complete shut-off. Valves suitable for most purposes are now available commercially. One design of high-pressure valve is shown in Figure 30, which is made to accommodate a variety of uses. These valves may be used up to 1700 atm.

A high-pressure valve of similar design is shown in Figure 31. A valuable feature of this valve is the shoulder cut on the valve stem so that the stem cannot be blown out of the valve body should the screw threads fail. This type of valve is applicable for pressures up to 4000 atm.

The Hofer valve was developed in Germany for high-pressure use. Two adaptations of this type of valve are shown in Figure 32. These valves are suitable for pressures up to 100 atm. For lower pressures, *e.g.*, 70–350 atm., valves are obtainable as standard items of manufacture from various suppliers.

(2) Fittings. It is customary to construct high-pressure transfer lines of cold-drawn seamless copper, mild steel, or high-tensile steel depending upon the application. Safe wall thickness of such tubing may be calculated by the methods described previously. In the case of copper or steel, the ratio of wall thickness to bore should equal 0.5 for pressures up to 300 atm. and 1.0 for pressures between 300–1000 atm.[74]

The design of connectors depends upon the material of the tubing and the working pressure. For copper tubing the design of Figure 33 is convenient. The tube is soft-soldered or brazed into a brass nipple and the seating of the nipple on a conical seating is obtained by tightening the nut. For steel tubing the design shown in Figure 34 can be utilized where the nipple is attached by a fine thread and silver soldering.

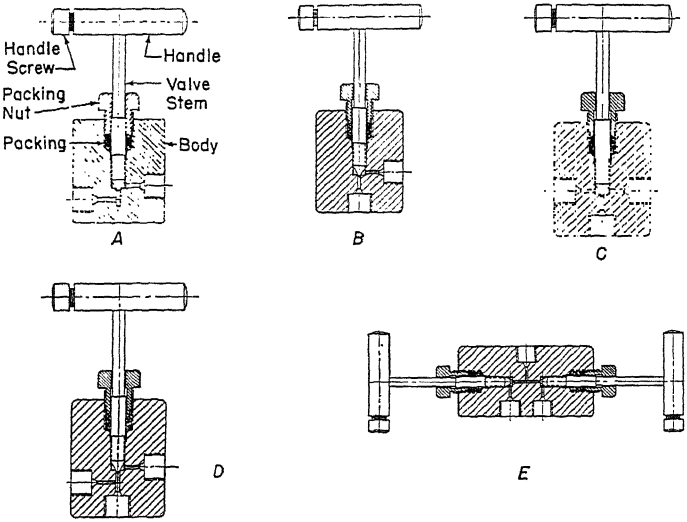

Fig. 30. High-pressure valves (1700 atm.): *A*, 2-way straight valve; *B*, 2-way angle valve; *C*, 3-way valve (cross type); *D*, 3-way valve (offset valve); *E*, combined inlet and bleeder valve. Courtesy *American Instrument Co.*

A standardized fitting is now available commercially as shown in Figure 35, for $\frac{1}{4}$, $\frac{3}{8}$, and $\frac{9}{16}$ in. O.D. tubing for pressures up to 1700 atm. The collar is attached with a left-hand thread to the tubing while the seal is obtained by screwing the gland into the body and pressing the conical end into a conical seat. Forming tools and

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[74] Newitt, *loc. cit.*, p. 91.

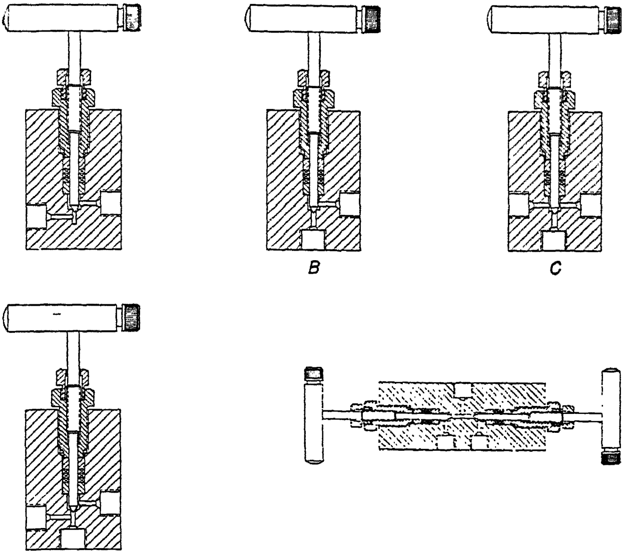

Fig. 31. High-pressure valves (4000 atm.): *A*, 2-way straight valve; *B*, 2-way angle valve; *C*, 3-way valve (cross type); *D*, 3-way valve (offset valve); *E*, combined inlet and bleeder valve. Courtesy *American Instrument Co.*

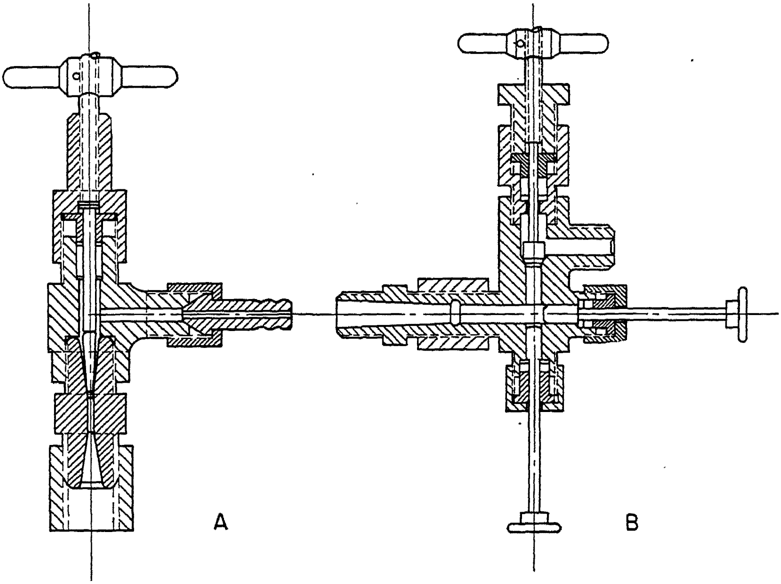

Fig. 32. A, Hofer valve for 1000 atmospheres; B, Hofer valve with cleanout plungers.

dies are available to make or renew the threads, conical ends, and conical seat.

To make connections, various standard high-pressure fittings are marketed as shown in Figure 36.

(3) Safety Devices. The failure of any part of high-pressure equipment is always a possibility and provisions should be made in order to localize the effects of such failure.

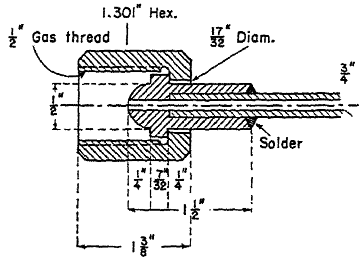

Fig. 33. Brass connector for copper tubing.[74]

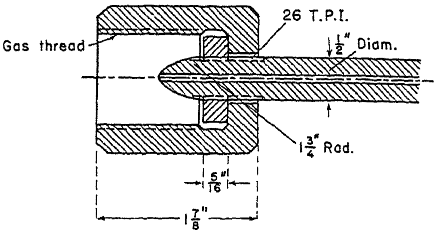

Fig. 34. Steel connector.[74]

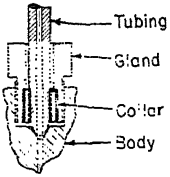

Fig. 35. Steel connector for application up to 1700 atmospheres. Courtesy *Autoclave Engineers, Inc.*

Failures in high-pressure processes due to abnormal stresses can be occasioned by: (*1*) the self-acceleration of an exothermic reaction, (*2*) local overheating upon active catalyst surfaces, and (*3*) accidental presence of impurities causing exothermic reactions. The dangers of corrosion, fatigue, and creep at elevated temperatures are also to be reckoned with in high-pressure work. It is imperative to incorporate devices for releasing pressure when a predetermined value is exceeded.

Safety releases are of two types—safety valves and rupture disks. The safety relief valve is best applied where a slow rise in pressure can be expected and where such occurrences are liable to be frequent. Most safety valves of the spring-loaded type suffer from the defect that they do not reseat properly. However, a design of the Fixed Nitrogen Research Laboratory has been found effective, Figure 37 illustrating the principles of the safety valve.[75] This device will relieve and reseat perfectly. For best results the valve should be protected by a filter assembly such as is shown in Figure 38.

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[75] Ernst and Reed, *Mech. Eng.*, **48,** 595 (1926).

The rupture disks serve to release the pressure of the system should the pressure rise to the danger point. Usually such devices are near the main reaction zone and the aperture should be sufficiently large. The design should incorporate a concentration of stress in a narrow ring of metal which is approximately the effective diameter of the disk. Two types are shown in Figure 39.

It should be emphasized that safety reliefs alone are not effective against all disruptive explosions. All possible precautions in the arrangement of vessels and pipe lines should be designed considering the eventuality of an explosion. Long runs of straight pipe should be avoided and heat-conducting screens to confine flame fronts should be placed at strategic points.

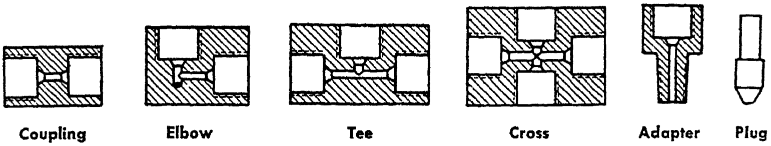

Fig. 36. Fittings for 1700 atmospheres. Courtesy *Autoclave Engineers, Inc.*

It is desirable to have the pressure apparatus within a protective enclosure. Such enclosure can suitably be made of mild steel plate backed by a layer of sand. All operating controls should be outside this chamber; pressure gages, flowmeters, liquid levels, etc., should be observed by means of mirrors or through narrow observation slits.

The safety screen should include an opening or weak area to allow the explosion wave to escape away from laboratory personnel. Instead of, or in addition to, doors, an explosion trap similar to light traps in darkroom entrances can be utilized to advantage

Where a high-pressure stall or chamber is not feasible, a protective screen woven from manilla rope and hung freely from overhead supports is effective against small fragments.

(4) Measurement of High Pressures. For pressure measurement some form of primary measurement should be available either for direct measurement or for calibrating a secondary gage.

Primary measurements are usually made by means of a *deadweight tester*. Pressure is transmitted by liquid pressure to the gage piston.

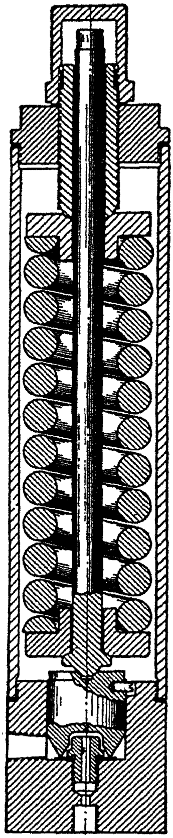

Fig. 37. Adjustable safety relief valve. Courtesy *American Instrument Co.*

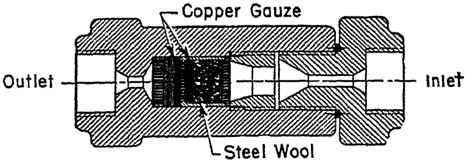

Fig. 38. Filter assembly. Courtesy *American Instrument Co.*

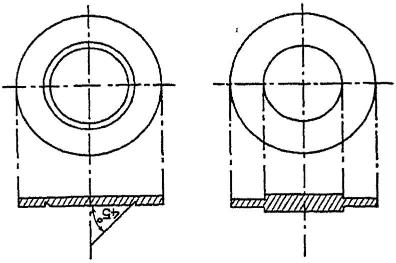

Fig. 39. Rupture disks.[74]

If the piston floats freely on the liquid and the cross-sectional area is known, then the total weight required to balance the liquid pressure can be used to calculate the gage pressure.

To avoid excessively large weights the piston diameter can be reduced. For work of high accuracy the piston must be rotated or oscillated.[76–78] Various corrections have to be applied to compensate for distortion of the cylinder walls due to pressure, increase in diameter due to temperature rise, and for the compressibility of the fluid. Some of these variables are best determined as gage factors in a calibration against a mercury column for an absolute determination. Further details are summarized by Newitt.[79]

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[76] Holburn and Schultze, *Ann. Physik*, **47,** 1095 (1915).

[77] Michels, *Ann. Physik*, **72,** 285 (1923).

[78] Keyes, *Proc. Am. Acad. Arts Sci.*, **68,** 505 (1933); *Ind. Eng. Chem.*, **23,** 1475 (1931).

[79] Newitt, *The Design of High Pressure Plant and Properties of Fluids at High Pressures.* Clarendon Press, Oxford, 1940, pp. 109–130.

Of the secondary pressure-measuring devices, the *Bourdon gage* is so widely applied that some discussion of its construction and limitations is warranted. The main element in this gage is the Bourdon tube which consists of a closed, metal tube, elliptical in section and bent to form a circular arc. One end of the tube is rigid and is attached to the pressure connection of the gage. The other end of the tube is closed and, upon application of an internal pressure, the tube tends to straighten and, being free and frictionless, the movement is proportional to the pressure. By means of mechanical gears, a pointer is moved over a calibrated dial.

For low pressures, the Bourdon tube is brass or bronze; for high pressures, plain or high-tensile steels are utilized. For extremely high pressure, a steel bar may be drilled and the outer surface machined to the requisite dimensions. After threading the ends, the main portion is flattened to an elliptical section, the tube being annealed and hardened before use.

The extreme range of a Bourdon gage is about 5000 atm., but at about 2000 atm., hysteresis effects occur and special precautions should be observed and frequent calibrations made against a primary standard.[80]

The standard form of a gage has a metal dial or face to which the Bourdon tube is attached. At the back of the dustproof casing, a hinged flap may be provided or the back itself may be of thin-gage metal to release any sudden pressure arising in the casing. The gage window should be transparent plastic or safety glass. The gage must be mounted in such a way that the back is free and flying fragments will not injure the observer.

High-pressure gas should never be suddenly admitted into a gage since the impact may cause injury to the gage, and, if adiabatic compression occurs, the subsequent temperature rise may give rise to an explosion. It is customary to provide a pinhole orifice in a small screw inserted inside the gage stem to minimize this hazard. In gages for use with oxygen it is imperative to have the gage as well as all parts of the system entirely free from oil. In this connection, the use of water-pumped nitrogen instead of oil-pumped nitrogen in high-pressure systems is emphasized.

A relatively new development in pressure measurement is the application of an unbonded resistance wire strain gage to measure the displacement of the center of a diaphragm.[81] Essentially, pressure causes a diaphragm to expand and the movement of the diaphragm causes an attached wire strain gage to change in resistance. By calibrating the resistance change against pressure, an accurate device for pressure measurement is obtained. Because of their high natural frequencies, these gages are extremely useful for recording rapidly fluctuating pressures. By appropriate electrical leads, pressure readings can be made from a safe location.[82]

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[80] Bridgman, *Proc. Am. Acad. Arts Sci.*, **44**, 201 (1909).

The most common and convenient pressure measuring device for extremely high pressures (*e.g.*, over 1000 atm.) is the change in resistance of manganin with pressure. With appropriate precautions the error with this method was found to be less than 1% at 30,000 atmospheres.[83]

F. BATCH SYSTEMS

For general laboratory work and exploratory investigations, the use of batch apparatus offers a wide degree of flexibility and utility. The apparatus varies with the needs of the catalytic reaction for intimate contact between reactants and catalyst. This is in distinction to noncatalytic reactions which are customarily conducted in a sealed tube. One or more autoclaves should be available in every well-equipped laboratory because of the important applications which can be made by means of catalysis. It is obvious that, by changing reactants and removing products continuously, autoclaves can be incorporated into continuous processes. For purposes of discussion we consider autoclaves according to the manner in which agitation is obtained.

(1) Rotating Autoclave. The first extensive use of high-pressure autoclaves was by Ipatieff whose work in this field dates from 1903. Ipatieff's autoclave (or bomb) consists of a forged cylinder equipped with a head secured to the body by means of an Ipatieff closure (mentioned previously). Agitation of the contents of the bomb is obtained by placing it in an inclined position and rotating slowly. An Ipatieff bomb shown in Figure 40, is particularly useful for exploratory work since it is relatively easy to open and clean.[84]

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[81] Meyer, *Instruments*, **19**, No. 3, 136–139 (1946).

[82] Obtainable from *Statham Laboratories*, Los Angeles, Cal.

[83] Bridgman, *Revs. Modern Phys.*, **18**, 1–93 (1946).

[84] Ipatieff, *Catalytic Reaction at High Pressures and Temperatures*. Macmillan, New York, 1936, pp. 31–33.

The hydrogenation of benzene in the Ipatieff bomb will serve to illustrate the use of this equipment. To 50 g. benzene is added 5 g. catalyst. The catalyst consists of 4 g. nickel oxide (obtained by ignition) and 1 g. reduced iron. About 100 atm. of hydrogen is pumped into a bomb of 850-ml. capacity. The autoclave is rotated and heated to 250°C., at which temperature it is held for 2 hours. A complete hydrogenation of benzene to cyclohexane takes place. If a precipitated nickel catalyst is used, a temperature of 100°C. can be employed.

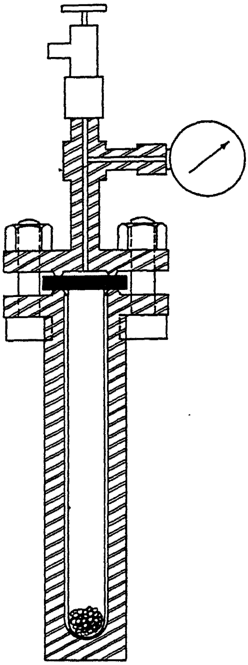

Fig. 40. Ipatieff autoclave.[84]

A similar autoclave has been developed by the Bureau of Mines[85] (see Fig. 29).

(2) Rocking Autoclave. The American Instrument Company has developed a series of shaking bombs which are satisfactory for catalytic hydrogenation and similar reactions. The ordinary bombs are constructed of a manganese-type steel containing 0.45% carbon, 1.40% manganese, 0.03% phosphorus, and 0.08% sulfur and are usually fitted with a glass or stainless steel liner to prevent corrosion. The arrangement of the bomb is shown in Figure 41. Bombs are constructed for working pressures up to 4000 atm. in sizes ranging from 25 ml. to 15 liters.

The assembly of a bomb is shown in Figure 42. The autoclave is held in place by a single bolt through the bottom of an outer heating jacket (not shown) and can be readily removed for cleaning. A metal and a glass liner for protecting the bomb interior are also shown in Figure 42. This type of equipment is particularly suited for catalytic hydrogenation. A detailed description and discussion of the use of this apparatus for hydrogenation is presented in the book of Homer Adkins.[86] For work on corrosive substances, the Ipatieff design is simpler and much easier to clean.

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[85] Clark, Golden, Whitehouse, and Storch, *Ind. Eng. Chem.*, **39,** 1555 (1947).

[86] Adkins, *Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts*. Univ. Wisconsin Press, Madison, 1937.

(3) Stirring Autoclaves. Most autoclaves derive agitation from the rotation of a stirrer although it is customary in large installations to obtain mixing and agitation by recirculation of the reaction mixture. Stirring autoclaves may be distinguished by the method of driving the stirrer, *i.e.*, external drive with stuffing box, external drive without stuffing box and internal drive.

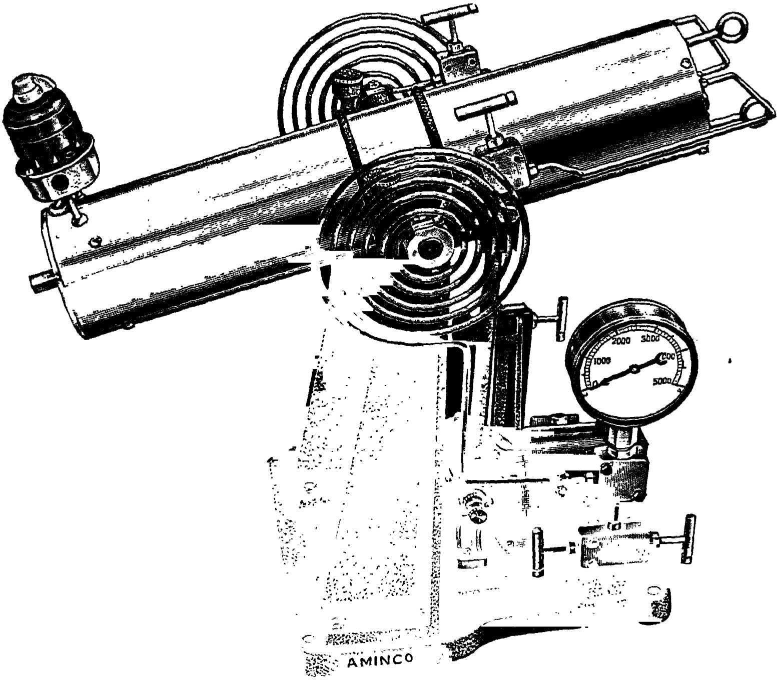

Fig. 41. Rocking autoclave. Courtesy *American Instrument Co.*

Externally Driven Stirring Autoclave. By far the most common method of obtaining agitation is by use of an external drive with a stuffing box. Exemplifying this type are the autoclaves designed at Teddington for the Chemical Research Laboratory (C.R.L.). Figure 43 shows the body and head of the autoclave while Figure 44 shows the stirrer shaft assembly for a 2-liter, 250-atm. autoclave.[87] About 0.3 horsepower is required to rotate the shaft at 150 r.p.m. The gage is protected from the contents of the autoclave by an oil seal which also serves to lubricate the shaft. Oil is prevented from entering the autoclave by leather washers below the lantern ring. Other sizes of autoclaves from 25 ml. to 12 liters have been made according to the same design.

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[87] Tongue, *The Design and Construction of High Pressure Chemical Plant.* Van Nostrand, New York, 1934, pp. 279–286.

Before the war, Andreas Hofer of Mulheim-Ruhr, Germany, had developed a series of stirring autoclaves designed for working pressures of 300 atm. The joint between the cover and body was obtained by a recessed gasket. The stirrer shaft was lubricated by an oil bottle maintained at the same pressure as that in the autoclave. This autoclave was gas heated but electrical heating was supplied in other designs.[88]

At the present time, two American companies are producing stirring autoclaves for laboratory use. The American Instrument Company fabricates bottom-stirred autoclaves. These have internal volumes ranging from 1 to 3 liters for pressures up to 680 atm. Figure 45 illustrates the general arrangement.

For working pressures up to 200 atm., Autoclave Engineers, Inc., has developed stirring autoclaves of 4-, 11-, and 19-liter sizes. These are equipped with a blowout pipe and a safety head. The stuffing box is water-cooled. The same company furnishes a 1-liter stainless steel autoclave for 135 atm. working pressure. This autoclave has an internal cooling coil and an outside equalizing oil cylinder. The top of the equalizing cylinder has a connection to the bomb interior through a valve; a connection from the bottom of the cylinder leads to the shaft packing lantern. Pressure is thus equalized between the autoclave and the packing lantern and the shaft packing seals against oil instead of gas, providing an efficient seal.

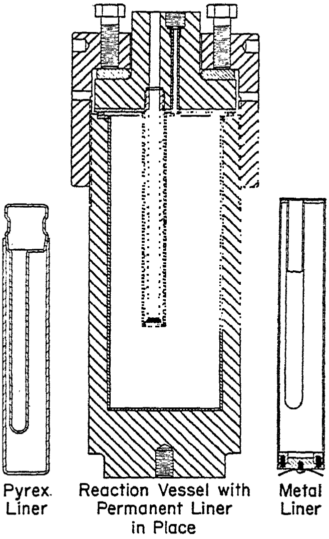

Fig. 42. Rocking autoclave assembly and liners. Courtesy *American Instrument Co.*

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[88] Eucken and Jakob, *Der Chemie Ingenieur*. Vol. III, Part 4, Akadem. Verlagsgesellschaft, Leipzig, 1939, p. 86.

Internally Driven Stirring Autoclave. With a stuffing box which must seal against high pressures, there are definite limitations as to the speed of rotation of the stirrer. To obviate this difficulty, it is possible to place the stirring motor within the high-pressure zone so that the only external connections needed are those to bring in electricity to operate the motor. Macmillan and Krase[89] describe an autoclave of this type which is shown in Figure 46. A 1750-r.p.m., 0.05-horsepower motor was utilized.

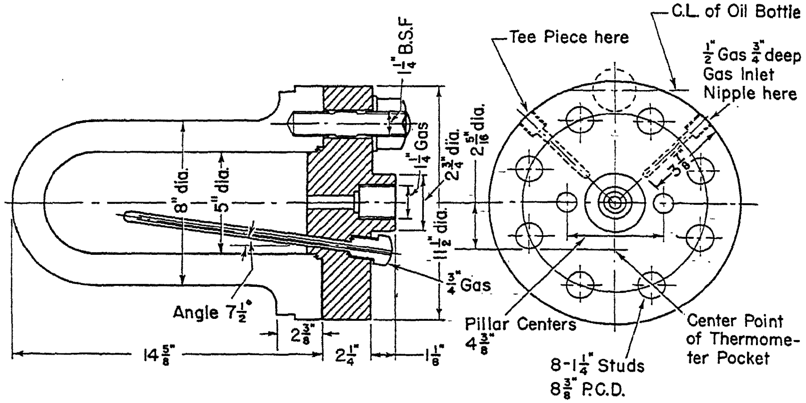

Fig. 43. Body and closure head of externally driven autoclave.[87]

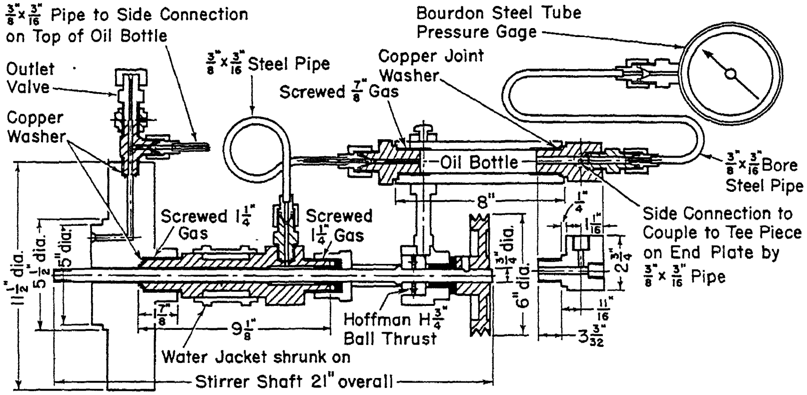
$\frac{3}{8}$"×$\frac{3}{16}$" Pipe to Side Connection on Top of Oil Bottle
Outlet Valve
Copper Washer
$\frac{3}{8}$"×$\frac{3}{16}$" Steel Pipe
Screwed $\frac{7}{8}$" Gas
Copper Joint Washer
Bourdon Steel Tube Pressure Gage
Oil Bottle
$\frac{3}{8}$"×$\frac{3}{16}$" Bore Steel Pipe
Side Connection to Couple to Tee Piece on End Plate by $\frac{3}{8}$"×$\frac{3}{16}$" Pipe
Screwed $1\frac{1}{4}$" Gas
Screwed $1\frac{1}{4}$" Gas
8"
$\frac{1}{4}$"
$1\frac{1}{16}$"
$2\frac{1}{4}$"
$\frac{11}{16}$"
$3\frac{3}{32}$"
$1\frac{3}{4}$" dia.
6" dia.
$11\frac{1}{2}$" dia.
$5\frac{1}{2}$" dia.
5" dia.
$1\frac{7}{8}$"
$9\frac{1}{8}$"
Hoffman H$\frac{3}{4}$" Ball Thrust
Water Jacket shrunk on
Stirrer Shaft 21" overall

Fig. 44. Stirrer assembly of externally driven autoclave.[87]

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[89] Macmillan and Krase, *Ind. Eng. Chem.*, 24, 101–102 (1932).

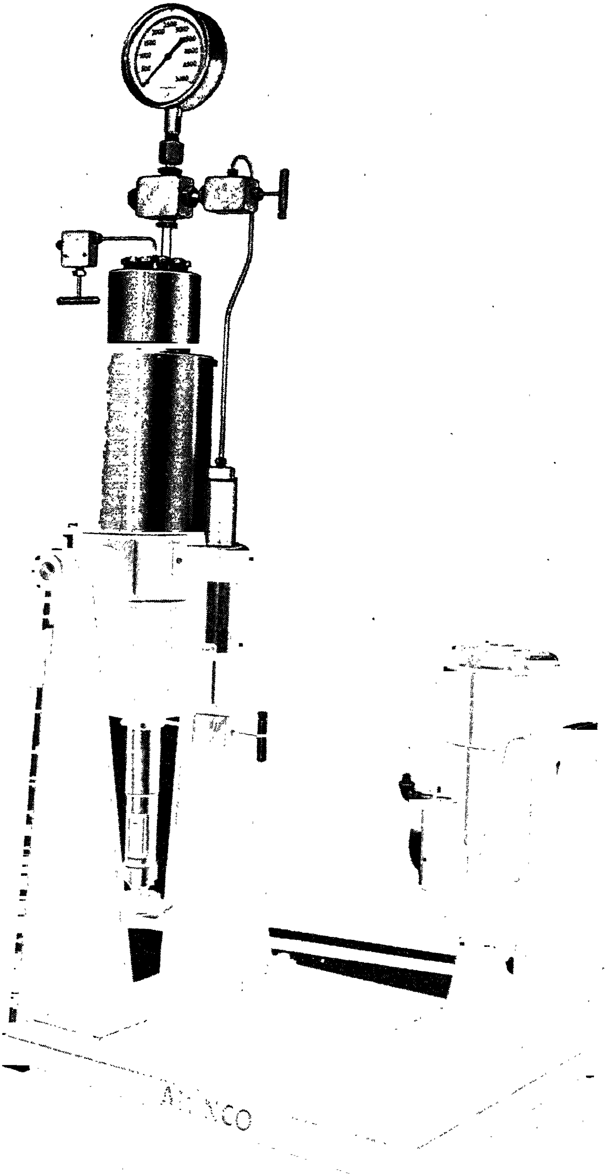

Fig. 45. Bottom-stirred autoclave in operating position.
Courtesy *American Instrument Co.*

The unit consists of three sections: a lower part or reactor (into which a 5 cm. diameter by 25 cm. glass test tube can be fitted), a middle part containing cooling water, and a top part containing the motor and electrical leads. The apparatus is suitable for temperatures up to 200°C. and for pressures to 300 atm.

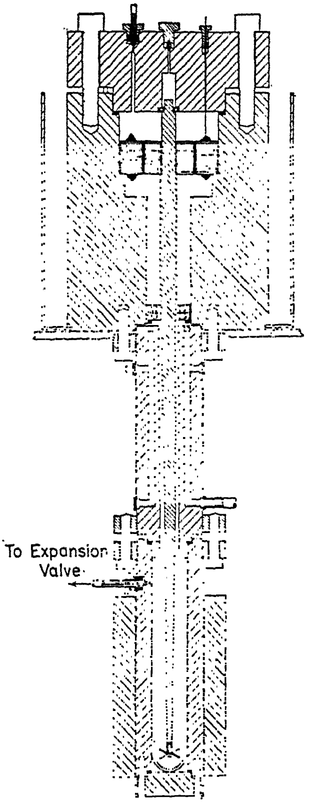

Fig. 46. Internal electric motor stirring autoclave.[89]

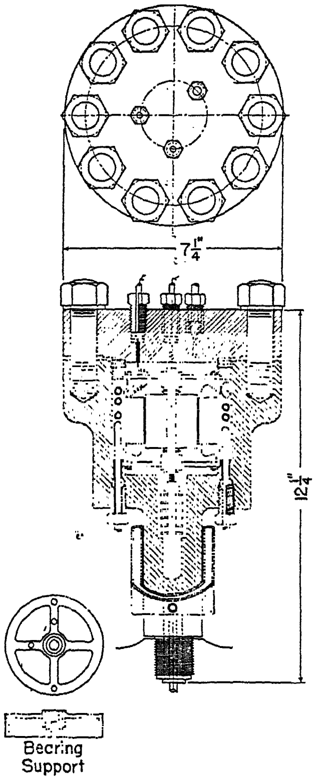

Fig. 47. Internally driven stirring autoclave.[90]

An internally driven agitator built to operate under severe conditions of temperature, pressure, and chemical attack has been described by Kiebler (Fig. 47).[90] The apparatus was designed for use in the Coal Research Laboratory at Carnegie Institute of Technology to study the hydrogenation of coal in aqueous alkali at temperatures up to 400°C. and pressures up to 400 atmospheres. The stirrer is driven by a 1/30 h.p. motor at about 1500 r.p.m. Cooling coils surround the motor stator. The entire assembly is screwed into a head which in turn is bolted to a reactor (not shown). The reactor used with the above stirrer assembly had an internal volume of 750 cc. in which a 5-cm. propeller was revolved at 1500 r.p.m.

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[90] Kiebler, *Ind. Eng. Chem.*, **37**, 538–540 (1945).

Externally Driven Stirring Autoclave Without Stuffing Box. One of the most recent developments is the use of an induction field to drive an armature contained in the high-pressure zone. This design was developed by the Universal Oil Products Company and is now available through Autoclave Engineers, Inc. A diagram of the unit is shown in Figure 48. A 1-horsepower motor is disassembled and the armature is enclosed in a stainless steel case. The rotating induction field outside the high-pressure vessel drives the stirrer at about 1725 r.p.m. The present design permits a working pressure of 80 atm. up to 250°C. The stirring is obtained by means of a 6.3 cm. diameter turbo impeller in a 1000-cc. stainless steel bomb. Smaller bombs of 500- and 250-cc. capacity are also available.

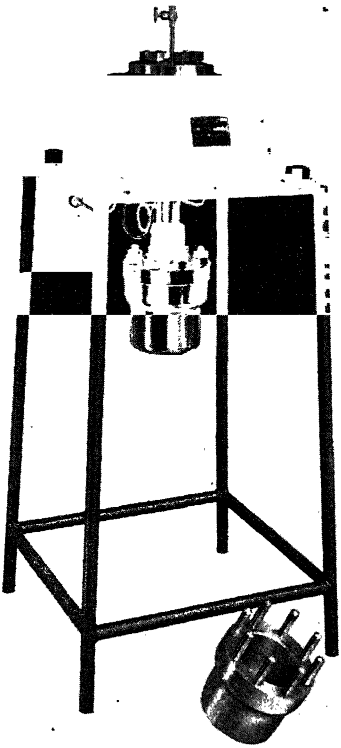

Fig. 48. Induction driven stirring autoclave. Courtesy *Autoclave Engineers, Inc.*

G. CONTINUOUS FLOW SYSTEMS

(1) Automatic Control. Because of the inherent dangers of high-pressure operation, remote automatic control of the ordinary variables, temperature and pressure, should be employed wherever possible. This is particularly important in continuous flow processes where automatic control of flow also is advisable. In batch operations where simplicity and flexibility of equipment is paramount, nonautomatic equipment may be justified. However, in general, uniformity of reaction conditions and safety of operation should far outweigh considerations of the additional cost of control instruments.

Temperature. Temperature measurement and control in high-pressure processes utilize standard devices which function independently of the process pressure. The subjects of temperature measurement and control and of heat transfer are treated elsewhere in separate chapters.[90a] The most important method of measuring and controlling temperature of high pressure catalytic apparatus depends upon the electrical potential generated by a thermocouple. This potential can be measured by means of a millivoltmeter or by a potentiometer type of instrument which may be used to actuate on-off or proportioning controllers. Choice of controller depends on the accuracy of temperature control required.[91]

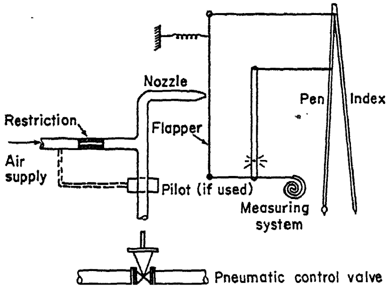

Fig. 49. Schematic representation of a pressure controller.[91]

A block furnace having automatic control and described under atmospheric pressure techniques is also suitable for use with high-pressure apparatus.

Pressure. Pressures are measured in continuous flow systems by the same devices as used in batch operations. To illustrate one type of system for the measurement and control of high pressure, reference is made to Figure 49. Pressure from the apparatus is conducted by means of high-pressure tubing to the measuring system which is usually a Bourdon tube. Pressure variations are indicated by the pen position. The index pointer sets the relative position of nozzle and flapper which determines the air supplied to the pneumatic control valve. The air pressure acts on a diaphragm which by reason of its large area permits a relatively small air pressure to counteract the high pressure exerted on the valve stem.

[90a] Egly, "Heating and Cooling," this series. Sturtevant, "Temperature Measurement" and "Temperature Control," in *Physical Methods of Organic Chemistry*, 2nd ed., Interscience; New York, this series.

[91] Eckman, *Principles of Industrial Process Control*. Wiley, New York, 1945.

Such valves are shown in Figure 50. The valve can operate at some point between fully open and fully closed; it is usually possible to hold the pressure within a fraction of 1% of the control point.

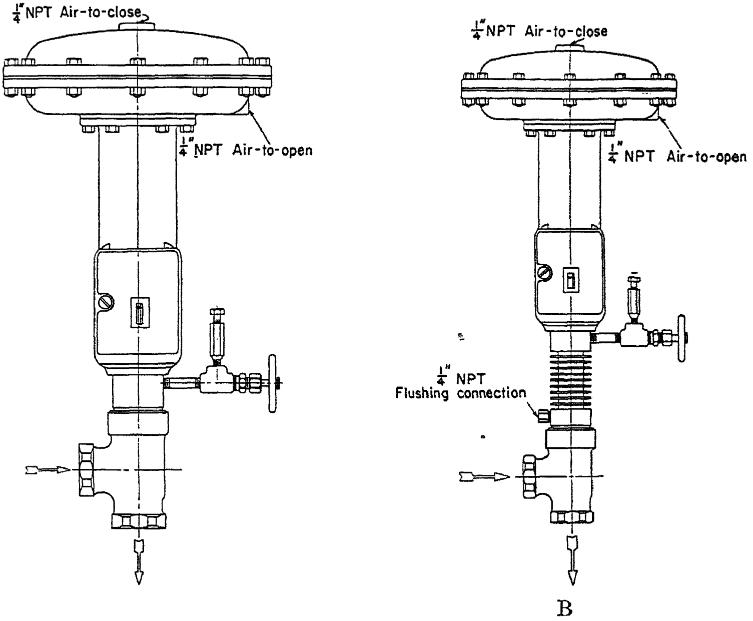

Fig. 50. Pneumatically operated pressure control valves. Courtesy *Mason-Neilan Regulator Co.*

Instead of pneumatic operation, an electric motor can be employed to drive the valve stem up and down. Devices utilizing a magnetic field to operate the system pressure (Figure 51) have been suggested.[92] By means of contact points attached to a Bourdon gage (Fig. 52) a magnet coil in the valve is energized to open the valve. Further discussion of the design of pressure controllers may be found in the book of Eckman.[93]

[92] Larson and Karrer, *Ind. Eng. Chem.*, **14**, 1012 (1922).
[93] Eckman, *loc. cit.*

Flowmeters. Flowmeters for measuring the rate of fluid flow in a pipe are usually of the differential type. However other types such as the volumetric or rotameter (area type) can also be adapted to high pressure flow measurement and control.

The differential flowmeter operates on the principle that there is a specific differential pressure for each rate of flow of fluid through a restriction. The restriction may be an orifice plate, a flow nozzle, or a venturi tube. For streamline flow, the rate of flow is proportional to the square root of pressure differential.

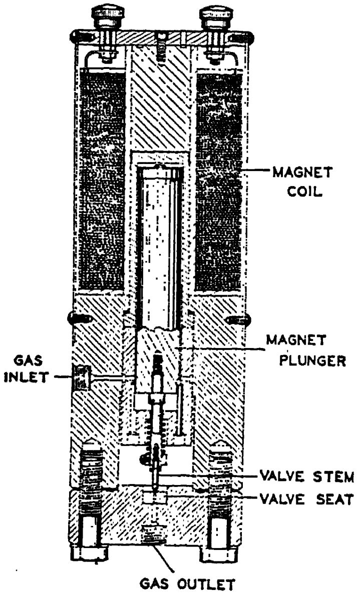

Fig. 51. Magnetic pressure regulating valve. Courtesy *American Instrument Co.*

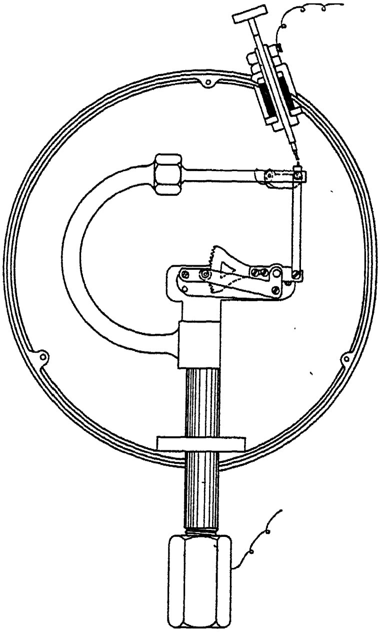

Fig. 52. Bourdon gage equipped for automatic pressure control.[92]

For an indication of flow the swinging U tube shown in Figure 53 may be of value.[94] To measure the differential pressure, the device illustrated in Figure 54 may be used.[94] The resistance of the wire in each tube indicates the height of mercury in the respective tubes.

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[94] Tongue, *The Design and Construction of High Pressure Chemical Plant.* Van Nostrand, New York, 1934, pp 83–84.

A flowmeter developed by Brady and Corson[95] measures the pressure drop across an orifice by electrical means (Fig. 55). The orifice consists of a longitudinal scratch on the surface of a cylinder which fits snugly in a steel barrel. The pressure drop across the orifice causes the left mercury leg to drop; the amount of this drop is indicated by increased resistance of a wire extending through the left leg. Flows of as low as 500 cc. per hour at normal temperature and pressure can be measured. The design shown is for 135 atm., but suitable modification the principle of construction could be extended to higher pressures.

Since the flowmeter produces a pressure differential, the problem of *pressure control* resolves itself to the measurement of the pressure differential. If the pressure differential is varied by the position of a flow valve, an automatic control from the pressure differential to the flow valve can be arranged.

Recently, the Fischer-Porter Company has developed area-type rotameters for measuring fluid flows at high pressure. A float is suspended in a tapered glass tube by the flow of fluid upwards, the height being dependent upon the rate, temperature, and other factors. The position of the float can be observed visually by means of an armored sight glass or magnetically in case glass cannot be used.

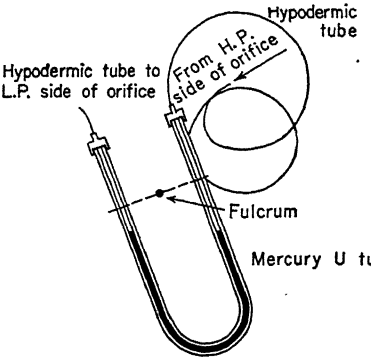
Hypodermic tube
From H.P. side of orifice
Hypodermic tube to L.P. side of orifice
Fulcrum
Mercury U tu

Fig. 53. Swinging U-type manometer.[94]

It is obvious that flow measurement is difficult at high pressures and, wherever possible, the usual expedient in the laboratory or small plant is to measure and control the flow rate at low pressure. Similarly if the material is a liquid at ordinary temperatures, a liquid pump coupled with a sight gage is quite satisfactory. Specific examples of such applications are presented in the next section.

Pumps and Compressors. In high-pressure flow processes it may be necessary to compress gas to high pressures and to pump liquid into a high-pressure system. In addition, recirculation of gases and liquids may be required in the process. It is not possible to enter into a detailed discussion of the design of compressors and pumps but a few remarks are appropriate.

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[95] Brady and Corson, *Ind. Eng. Chem., Anal. Ed.*, 14, 656–657 (1942).

In compression of gases to high pressures it is customary to perform this in a multistage machine. This is necessary to: (*1*) reduce the operating temperature by cooling between the intermediate stages; (*2*) decrease the work required for compression (lower horse power); and (*3*) diminish bearing loads and stress requirements in the design of the compressor.

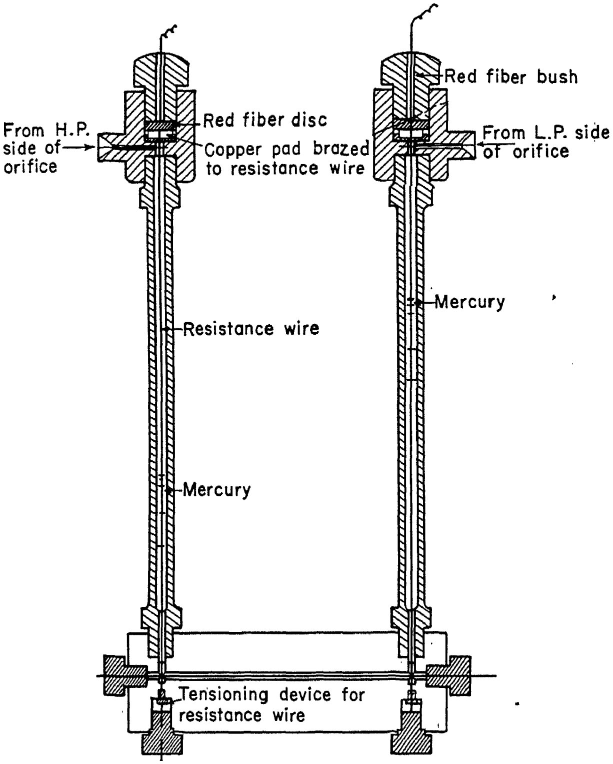
Red fiber bush
From H.P. side of orifice
Red fiber disc
Copper pad brazed to resistance wire
From L.P. side of orifice
Mercury
Resistance wire
Mercury
Tensioning device for resistance wire

Fig. 54. High-pressure orifice flowmeter.[94]

Examples of small compressors suitable for laboratory or pilot plant work are the Rix and Norwalk compressors.[96] The Rix com-

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[96] Available from *American Instrument Co.*, Silver Spring, Md.

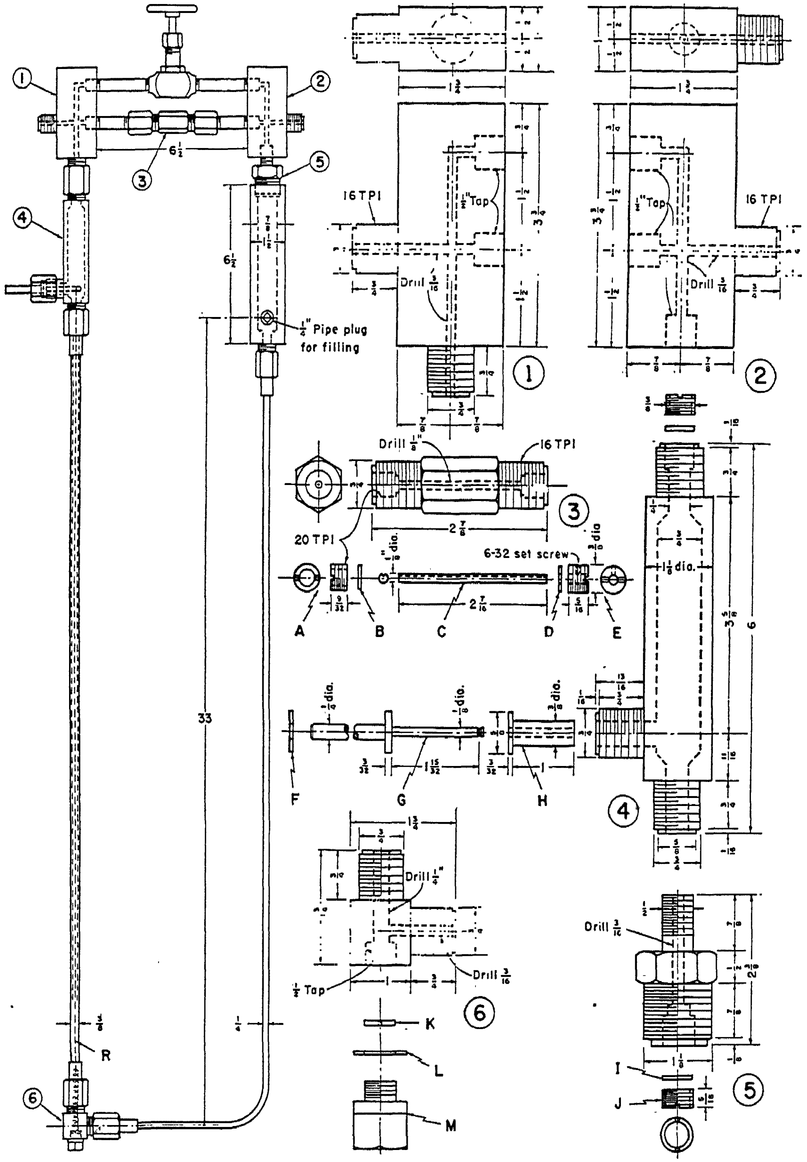

Fig. 55. High-pressure flowmeter.[95]

pressor is of the three-stage type and is equipped with a valve system of the steel-disk poppet type to operate up to 340 atm. pressure; 5–10 horsepower is required. The Norwalk compressor is of the five-stage type and will produce a maximum pressure of 1000 atm. A more extensive discussion is given in the book of Tongue.[97]

For pumping liquids into high-pressure systems, piston displacement pumps are quite satisfactory for pilot plant or laboratory installations. These pumps may be the duplex type as shown in Figure 56 so that either one or two liquids can be pumped simultaneously. Flow rates can be changed independently by adjustment of the stroke by means of a micrometer adjustment. A cooling jacket should be provided so that volatile liquids or compressed gases, such as propane, can be pumped without vapor lock difficulties. Double, stainless steel check valves are provided for each piston.

For pumping corrosive liquids, sludges, and pastes, a diaphragm arrangement instead of a piston eliminates packing difficulties. The suction and discharge pressure is transmitted from a confined liquid through a diaphragm to the fluid to be pumped. Adjustment of the stroke of the piston in contact with a confined fluid permits changes of the flow rate.[98]

For gas circulation at high pressures a single-stage compressor is sufficient since in most cases it is merely necessary to overcome the friction (*e.g.*, pressure drop through a catalyst bed) of the system. This subject is described in greater detail by Tongue.[99]

A charging device[100] which can be utilized to compress gases in amounts sufficient for laboratory purposes is shown in Figure 56. This system does not require a compressor since the gas is compressed by pumping water into the gas charger. Two or more gases can be mixed and compressed by means of the hydraulic pumps. The rate of feeding a gas under high pressure can be measured accurately by measuring the water discharged from the water-feed burets. If the gases react with water, other fluids, such as hydrocarbon oil, glycerin, or silicone, can appropriately be employed.

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[97] Tongue, *loc. cit.*, pp. 36–72.

[98] Wilson Pulsafeeder Proportioning Pump made by *Lapp Insulator Co.*, Leroy, N. Y.

[99] Tongue, *loc. cit.*, pp. 73–83.

[100] Ipatieff, Monroe, and Fischer, Petroleum Division, American Chemical Society, New York, Sept. 15–19, 1947; *Ind. Eng. Chem.*, Nov., 1948.

(2) Catalyst Tubes. In general the design of catalyst tubes parallels the design of the autoclaves. However, it is usually convenient to have a movable closure on each end to facilitate charging and removing catalyst and for cleaning purposes. A few examples will serve to illustrate the elements which are needed for a catalyst tube.

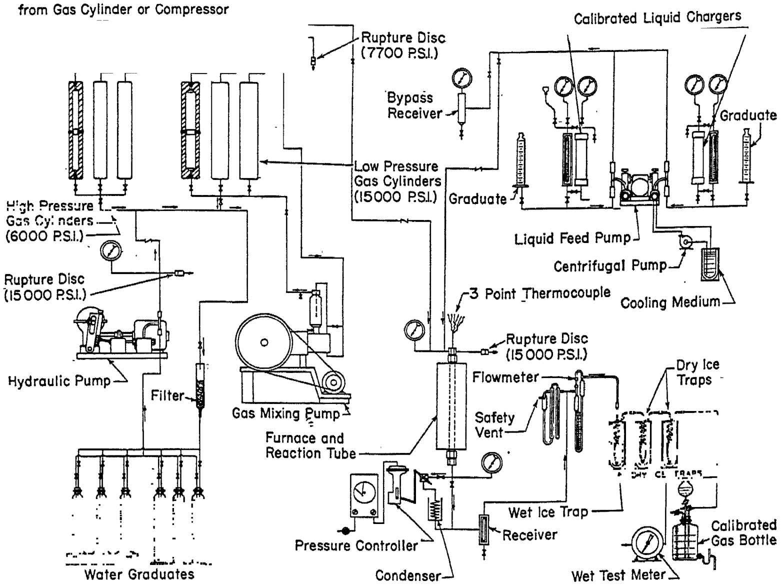

Fig. 56. Diagram of superatmospheric flow apparatus.[100]

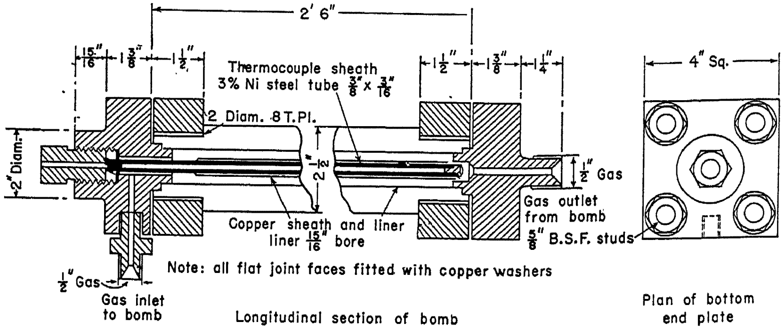

Fig. 57. High-pressure catalyst tube.[101]

Tongue[101] described a 1-inch tube which was used for methanol synthesis at the Chemical Research Laboratories (Fig. 57).

This tube is of nickel–chrome–molybdenum steel and contains a copper liner; it is 76 cm. long. The ends are secured by 10 cm. square flanges. The temperature of the catalyst mass is determined by moving a thermocouple within the catalyst tube.

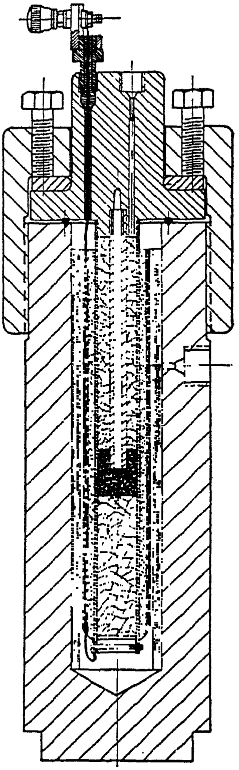

Fig. 58. High-pressure catalyst reactor tube with internal heating. Courtesy *American Instrument Co.*

For certain types of reactions it is advantageous to employ *internal heating.* An apparatus for pressures up to 1500 atm. and temperatures up to 500–600°C. is shown in Figure 58. Inside the chamber, a 2.5 by 24 cm. "test tube" contains the catalyst. An Alundum tube with an embedded heating coil surrounds this tube while a Pyrex tube forms an outer jacket for the assembly and serves also as an insulator to prevent excessive heating of the steel wall of the chamber. Gas enters at the side, passes upward between the chamber wall and the glass liner, down across the heating coil to the bottom, and up through the hot catalyst from which it passes out through the top.[102]

(3) Assembled Systems. As a specific example of high-pressure flow apparatus, the arrangement shown in Figure 59 has proved of value. The liquid feed is contained in a calibrated high pressure liquid charger equipped with a sight gage. The flow of liquid into the system is obtained by applying sufficient pressure above the liquid in the charger. In addition, an adjustable stroke liquid pump can be included. The gas flow into the reactor tube is observed by means of a flowmeter. Gas or liquid or both pass into the reaction tube contained in an aluminum–bronze block furnace. The reactants issuing from the tube are maintained at constant pressure by means of a pressure controller.

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[101] Tongue, *loc. cit.*, p. 320.

[102] Available from *American Instrument Co.*, Silver Spring, Md.

The collection of liquid and gas is performed at atmospheric pressure in an appropriate condensing and metering system.

To illustrate one application of the use of this apparatus, the polymerization of propylene to liquid polymers may be cited. The catalyst is "solid phosphoric acid" prepared by impregnation of kieselguhr with 85% liquid phosphoric acid and drying of the resultant paste at 300°C. to a moisture content of 10–15%. At a temperature of 200°C. and a pressure of 10 atm., a space velocity of 1.0 volumes of liquid propylene per hour per volume of catalyst results in a 90% conversion of propylene to liquid polymers.

A second example[103] of high-pressure flow apparatus is shown in Figure 60. The arrangement has two unique features worthy of special notice. One feature is the provision for maintaining the pressure of liquefied gas constant by immersion of the gas cylinder in a thermostat. Constant pressure drop across a capillary in a line to the reactor provides constant flow of gas. The second feature is the use of the solubility of the catalyst (aluminum chloride) in the liquid charge (hydrocarbon) as a means of adding catalyst. Liquid from the charger is pumped by means of the pump through a saturator containing catalyst in lump form. By varying the temperature of the saturator, different amounts of catalyst can be added.

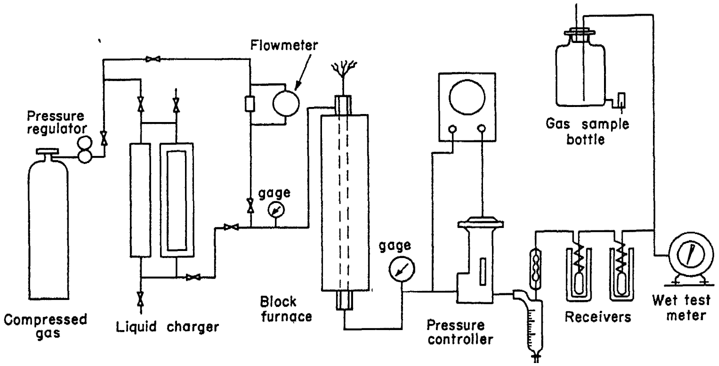

Fig. 59. High-pressure flow apparatus (Illinois Institute of Technology, Catalysis Laboratory).

As an example of the application of various high-pressure techniques in a flow apparatus, the installation of Ipatieff, Monroe, and

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[103] Mavity, Pines, Wackher, and Brooks, Petroleum Division, American Chemical Society, New York, Sept, 15–19, 1947.

Fischer[104] is described here in some detail (Fig. 56). The apparatus was designed to process normally liquid or gaseous reactants or combinations of both at pressures up to 900 atm. and at temperatures up to 565°C. The high-pressure plant was completely enclosed within steel barricades, approximately 6.5 mm. thick.

The apparatus essentially consists of six parts as follows. (*1*) A high-pressure gas charging system is comprised of six high-pressure cylinders, the top outlets being manifolded into a gas feedline. The bottom inlets may be connected to any one of 6 water graduates by a variable stroke hydraulic pump. The function of the pump is twofold: (*a*) by forcing water into the gas cylinder, it can increase the pressure up to 900 atm.; and (*b*) by pumping water in at a constant rate, gas can be withdrawn at any desired pressure into the gas feedline. (*2*) A gas mixing pump is provided so that gas mixtures can be prepared under high pressure. (*3*) The liquid charging system consists of two high pressure calibrated chargers for containing liquid of high vapor pressure and an adjustable stroke, liquid feed pump provided so that two separate liquid streams can be pumped, simul-

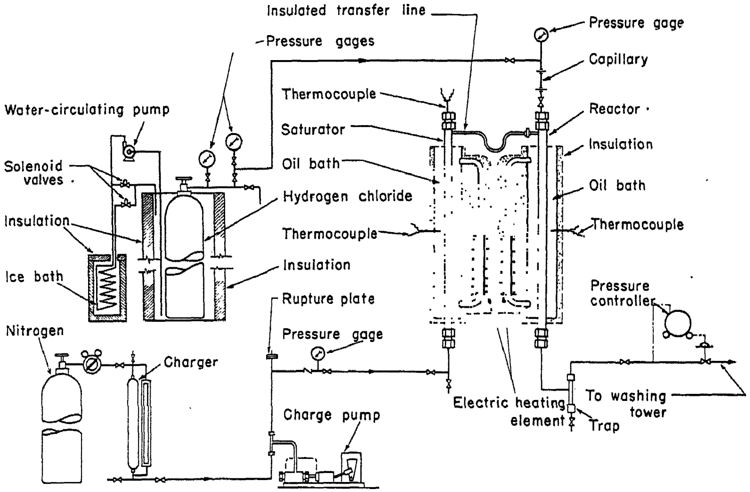

Fig. 60. High-pressure flow apparatus.[103]

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[104] Ipatieff, Monroe, and Fischer, Petroleum Division, American Chemical Society, New York, Sept, 15–19, 1947.

taneously, into the liquid feedline. Two glass graduates are also available for containing low vapor pressure liquids. (*4*) A copper-lined, high-pressure reaction tube is supported in a stainless-steel block furnace equipped with an automatic temperature regulator. (*5*) A pressure controller is provided at the exit end of the reactive tube for releasing the products to atmospheric pressure before condensation. (*6*) The collection part of the system is at atmospheric pressure and collects products with water, ice, and Dry Ice condensers.

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PHOTOCHEMICAL REACTIONS

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University of Rochester, Rochester, New York

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I. INTRODUCTION

1. Usefulness of Photochemical Reactions

Photochemical reactions will be of use to the synthetic organic chemist if one or the other of the following conditions is fulfilled: (*1*) The number of molecules reacting per quantum of light absorbed is quite large. This condition is met only for reactions which are decidedly exothermic and for which, moreover, there is no single step which is prohibited from having a high reaction velocity constant. These reactions are commonly referred to as chain reactions. (*2*) Products can be synthesized either more easily or in a higher state of purity than by any other means. Photochemical methods may be useful, even though the energy cost is high and the time consumed may be long. (*3*) Light energy is available and inexpensive. Even though (*1*) and (*2*) are not fulfilled, photochemistry may still prove useful under such conditions. This statement applies particularly to those reactions which can be carried out in sunlight in climates where the sunlight can be relied upon.

There are a few instances, examples of which will be cited in this chapter (page 126), in which photochemical reactions lead to unusual reactions which are not commonly encountered when more customary means are employed. Generally speaking, however, products obtained photochemically may also be obtained by other methods, and the usefulness of the photochemical approach will be based mainly either on convenience or on purity of the product. In certain instances the organic chemist may employ photochemical methods as an aid in establishing reaction mechanisms.

2. Limitations of Light Sources and Reaction Vessels

The usefulness of photochemical reactions is determined, to some extent, by the availability of suitable reaction vessels and light sources. Infrared radiation produces little or no effect in any chemical system except to raise the temperature. Visible light (approximate range 7000 to 4000 angstrom units) will frequently, if absorbed, produce chemical changes. Soft glass transmits the visible satisfactorily, but stops transmitting at about 3500 Å. Pyrex glass is practical to about 3000 Å., and certain special glasses are good for a few hundred angstrom units more. Fused quartz in small thickness (about 1 mm.) may transmit as far as 1650 to 1700 Å., but ordinary quartz apparatus cannot be relied upon beyond 2000 Å. For still shorter wave lengths the oxygen of the air is opaque, and a few substances, such as CaF_2 and LiF, may be used for windows, but this region of the spectrum is of interest mainly to the specialist and not to the chemist who mainly desires to carry out reactions.

II. GENERAL CONSIDERATIONS

Photochemical reactions may be classified as direct or sensitized. In a direct photochemical reaction one or more of the substances undergoing reaction absorb the light. In a sensitized reaction some substance absorbs light and induces reactions in which it does not participate as one of the disappearing molecules. Examples of sensitized reactions are: (*a*) the hydrogenation of ethylene in the presence of mercury vapor using radiation absorbed only by the mercury vapor; (*b*) the growth of plants due to radiation absorbed by the chlorophyll even though the latter undergoes no permanent chemical change; and (*c*) the oxidation of tetrachloroethylene to trichloroacetyl chloride by oxygen in the presence of chlorine and light absorbed only by the chlorine.

The study of photochemical reactions may be divided into two main parts: (*1*) a study of the immediate effect of the light on the absorbing molecule, *i.e.*, the primary process; and (*2*) a study of the reactions of the molecules, atoms, or radicals produced by the primary process.

1. Primary Process

When a molecule absorbs light, it is placed in a situation such that it is no longer in thermodynamic equilibrium with its surroundings, and hence it must lose energy in one of the three following forms: (*1*) fluorescence or phosphorescence, *i.e.*, all or part of the energy is re-emitted as radiant energy after a time interval which is usually a small fraction of a second but which may, in some cases, be much longer; (*2*) as chemical energy, *i.e.*, by the transformation of the starting materials into new compounds; and (*3*) as thermal energy resulting in increase in temperature of the reaction system or in loss of energy to the surroundings.

2. Secondary Reactions

Energy-rich atoms produced by the absorption of light may lose energy by collision with other molecules, thereby initiating chemical reactions. Thus, excited mercury atoms cause the dissociation of molecular hydrogen, inducing certain hydrogenation reactions. Similar collisions by energy-rich diatomic and polyatomic molecules must occur, but experimental data on such molecules are unsatisfactory. Often such molecules dissociate into atoms or molecules, and even in cases where they act as sensitizers, the reaction occurs in a series of steps which eventually lead to the resynthesis of the absorbing molecule.

Diatomic molecules may either be activated or dissociated depending on the wave length. The resulting atoms start other processes which may lead to large yields or small yields depending on circumstances. Two examples will be cited. When Cl_2 absorbs light below about 5000 Å. in wave length, chlorine atoms are formed. In the presence of hydrogen we have the following reactions:

$$Cl_2 + \text{quantum} \rightarrow 2\,Cl \tag{1}$$

$$Cl + H_2 \rightarrow HCl + H \tag{2}$$

$$H + Cl_2 \rightarrow HCl + Cl \tag{3}$$

$$Cl + Cl \rightarrow Cl_2 \tag{4}$$

Reactions (2) and (3) both occur as rapid reactions and since a new chlorine atom is formed for each one entering into reaction (2), they constitute a "chain" which continues until accidentally two chlorine atoms combine according to reaction (4). Thus many molecules of HCl, sometimes as many as 10^6, may be formed per quantum absorbed.[1] Of course the over-all reaction is exothermic, or this could not happen.

Another type is found with HI, which absorbs at 2500 Å. and below.[2] Here the first step is:

$$HI + \text{quantum} \rightarrow H + I \tag{5}$$

and this is followed by:

$$H + HI \rightarrow H_2 + I \tag{6}$$

$$I + I \rightarrow I_2 \tag{7}$$

This is not a chain reaction because the step which would produce a second hydrogen atom is:

$$I + HI \rightarrow I_2 + H \tag{8}$$

and this reaction is so endothermic as to be immeasurably slow. Consequently a chain cannot be propagated, and one molecule of hydrogen and one molecule of iodine represent the maximum yield per quantum.

Similar phenomena are observed with polyatomic molecules, although the difficulties of interpretation are much greater. Atoms and free radicals may result when such molecules absorb light, and chains may or may not be produced according to the reactions such atoms or molecules undergo.

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[1] Bodenstein, *Sitzber. preuss. Akad. Wiss.*, **1912**, 333.

[2] Warburg, *Sitzber. preuss. Akad. Wiss.*, **1918**, 300. Lewis, *Proc. Natl. Acad. Sci.* (*U. S.*), **13**, 720 (1927).

Acetaldehyde at 100°C. or more in the gas phase undergoes a chain decomposition[3] which may possibly be represented by the series of reactions:

$$CH_3CHO + \text{quantum} \rightarrow CO + CH_3 + H \tag{9}$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3 + CO \tag{10}$$

$$CH_3 + H \rightarrow CH_4 \tag{11}$$

The chain-propagating step is (10), and the chain-stopping step is (11). However, other processes go on simultaneously, and it should not be thought that (9), (10), and (11) represent the full story of acetaldehyde decomposition.

On the other hand, ketene decomposition seems to follow the sequence:[4]

$$CH_2CO + \text{quantum} \rightarrow CH_2 + CO \tag{12}$$

$$CH_2 + CH_2 \rightarrow C_2H_4 \tag{13}$$

and 1/2 C_2H_4 and CO are produced per quantum. There may be a small amount of reaction of methylene radicals:

$$CH_2 + CH_2CO \rightarrow C_2H_4 + CO \tag{14}$$

which would lead to a maximum formation of $2\,CO + 1\,C_2H_4$ per quantum. Actually about 1.1 molecule of CO are formed per quantum, but no indications of chains are found.

Many reactions which have low yields at low temperatures become chain reactions at high temperatures.

3. Monatomic Gases

We shall consider first the absorption of light by single atoms, *i.e.*, by monatomic gases. Isolated atoms show very simple absorption spectra, consisting of single lines usually relatively widely separated as to wave length. Monatomic gases, if pure, undergo no permanent chemical change following the absorption of radiation. The energy absorbed can reappear only as fluorescence or heat.

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[3] Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934). Blacet and Heldman, *ibid.*, **64**, 889 (1942). Blacet and Loeffler, *ibid.*, **64**, 893 (1942).

[4] Norrish, Crone, and Saltmarsh, *J. Chem. Soc.*, **1933**, 1533; *J. Am. Chem. Soc.*, **56**, 1644 (1934). Ross and Kistiakowsky, *ibid.*, **56**, 1112 (1934).

Only the following monatomic vapors need to be considered from the standpoint of practical photochemistry in the gas phase: mercury, cadmium, zinc, and xenon. The wave lengths of the absorption lines and the corresponding energies per gram atom are given in Table I. The energies are obtained from the formula $2.8577 \times 10^8/\lambda$ cal., where λ is the wave length in angstrom units, and 1 angstrom unit $= 10^{-8}$ cm.

REACTIONS SENSITIZED BY MONATOMIC GASES

When any of the lines in Table I are absorbed by the corresponding elements in the gas phase, the individual atoms possess, per gram atom, amounts of potential energy as indicated. This energy may be released upon collision with other molecules, or it may reappear as fluorescent radiation. If the energy is released to other molecules, part or all of it may be used to produce chemical changes. Thus a mercury atom which has absorbed the 2537.5 Å. line would be capable of inducing changes in molecules with which it collides providing such changes do not require more than 112,620 cal. per gram molecule for their initiation. Hydrogen molecules, which need only 103,000 cal. per gram molecule for dissociation into atoms, may be dissociated by impact with mercury atoms which have absorbed either of the lines indicated, with cadmium atoms which have absorbed the 2288.7 Å. line, with zinc atoms which have absorbed the 2139.3 Å. line, and by xenon atoms which have absorbed either of

TABLE I

Absorption Lines and Energies of Some Elements[5]

Element	Line, Å.	Energy, cal.	Element	Line, Å.	Energy, cal.
Hg	2537.5	112,620	Zn	3076.8	92,880
	1849.6	154,500		2139.3	135,580
Cd	3261.9	87,610	Xe	1491.0	191,660
	2288.7	124,860		1469.6	194,450

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[5] *Cf.* Bacher and Goudsmit, *Atomic Energy States.* 1st ed., McGraw-Hill, New York, 1932.

the two lines indicated. In some instances, however, other lines may be useful. For example, a cadmium atom which has absorbed the 3261.9 Å. line may undergo the reaction:

$$Cd + H_2 \rightarrow CdH + H \tag{15}$$

thus producing hydrogen atoms.[6] The heat of formation of CdH when added to the energy available from the excited cadmium atoms is sufficient to permit this reaction to occur.

Many reactions may be initiated by the action of these excited atoms. Thus the heat of dissociation of the carbon-hydrogen bond in most aliphatic hydrocarbons is approximately 100,000 cal. (see page 88), and excited mercury atoms, as well as several of the others, are capable of inducing the reaction $RH \rightarrow R + H$. Only in the case of methane does this reaction seem to be relatively improbable.

The carbon-carbon single bond requires roughly 80,000 cal. per gram molecule for its dissociation. Although there may be steric reasons which render dissociation of this bond by excited mercury atoms improbable in some molecules, there is ample energy available for it to occur.

4. Diatomic Molecules

With diatomic molecules the situation following absorption of light is definitely more complex. The energy of a diatomic molecule may, for purposes of our discussion, be divided into three parts: electronic, vibrational, and rotational. If, when a molecule absorbs radiation, it possesses enough energy to dissociate, such dissociation may follow. If the dissociation follows soon enough after the act of absorption, *i.e.*, in a period shorter than that required for one rotation, the spectrum will not possess definite lines or bands since the kinetic energies of the two atoms as they fly apart are not quantized and may assume arbitrary values. If the molecule after absorption of light stays together long enough to execute several rotations before it dissociates, the spectrum may consist of definite lines or bands. The appearance of the spectrum is not always a definite clue as to whether or not dissociation occurs, although one may state that a definitely continuous spectrum necessarily means dissociation.

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[6] *Cf.* Steacie, *Atomic and Free Radical Reactions.* Reinhold, New York, 1946, p. 31.

The main diatomic molecules of photochemical interest are the halogens for which the information in Table II is pertinent.[7]

The disagreement between the calculated wave length required to produce dissociation and the beginning of continuous absorption arises from the fact that when these molecules absorb light, they produce two atoms each, one of which is normal and the other of which is at an energy level greater than normal. The one with the larger amount of energy will probably lose its excess energy quite quickly on colliding with other molecules.

Molecules which absorb light at wave lengths longer than those required theoretically to produce dissociation, may ultimately dissociate. Thus bromine in the region between 5107 and 6320 Å. undoubtedly dissociates a fair fraction of the time, although every molecule which absorbs light below 5107 Å. in wave length dissociates immediately. When halogen molecules are dissolved in some solvent, the effect of light is similar to that in the gas phase except that the two atoms produced by the absorption of a quantum are walled in by solvent molecules to such an extent that they often recombine quite rapidly unless some other molecule is available with which they can react. Thus, while continuous absorption in the gas phase implies one dissociation per quantum absorbed, the effective number in the liquid phase may, under some conditions, be less.

TABLE II

Absorption and Energy Data of Halogens

Molecule	Heat of dissociation, cal.	Calculated maximum wave length for dissociation, Å.	Observed beginning of continuous absorption, Å.
Cl_2	56.9	5020	4785
Br_2	45.2	6320	5107
I_2	35.4	8070	4989

Diatomic molecules other than halogens which might be useful photochemically in the gas phase are *oxygen* and *carbon monoxide*.

5. Polyatomic Molecules

In polyatomic molecules many kinds of vibrations are possible, the number being generally $3n - 6$ where n is the number of atoms.

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[7] Sponer, *Molekülspektren*. Vol. I, Springer, Berlin, 1935.

Moreover, with many kinds of bonds present there will be many different energies of dissociation. Truly continuous absorption cannot occur at a wave length longer than that corresponding to the least energy required to produce some type of dissociation. Dissociation may involve rupture of some one bond, *e.g.*, $CH_3COCH_3 \rightarrow CH_3 + CH_3CO$, or it may result in formation of completed molecules, *e.g.*, $CH_3CHO \rightarrow CH_4 + CO$. The energy required for the latter type of process is almost invariably much smaller than for the former.

The energy required to break a carbon-hydrogen bond varies to some extent from one molecule to another, but usually lies between 90 and 100 kcal. Thus wave lengths longer than about 3000 Å. will be unable to cause any organic molecule to split off a hydrogen atom unless the temperature is so high that the thermal energy resident in the molecule contributes to the process. The carbon-carbon single bond also varies undoubtedly from molecule to molecule but usually requires 80 to 85 kcal. for its dissociation. This corresponds to a wave length of roughly 3500 Å. Carbon-carbon double bonds and carbon-oxygen bonds in aldehydes and ketones require so much energy for their dissociation that wave lengths near the limit of those transmitted by quartz would be necessary.

With simple polyatomic molecules a reasonably good guess can be made as to where a split will occur following absorption by light. The guess is based partly on energies required to break bonds, partly on steric considerations, but mainly by analogy with carefully studied cases. Complex molecules must be treated as individual cases for which general rules have not yet been formulated. A molecule which possesses a total energy, received from the light plus any thermal energy it may have possessed prior to absorption, great enough to permit several different modes of dissociation may react in more than one way. Indeed, one mode may not be favored strongly over the others. Thus, a photochemical reaction may be less specific than a thermal reaction of the type involving two reactants, although straight pyrolytic reactions may be equally complex.

III. LIGHT SOURCES

1. General

Light sources for photochemical work may be needed for the following purposes: (*1*) for the study of absorption spectra; (*2*) for the study of the mechanisms of reactions; and (*3*) for carrying out reactions on a scale such that the magnitude of the yield is important. Photochemical reactions (*2*, *3*) may require light sources of considerable *intensity*. Moreover, the choice will depend on the *chemical nature of the reactant.*

A. INTENSITIES NEEDED

If 10^{17} quanta are obtained per second at the proper wave length through whatever monochromating device is used, it is evident that 6×10^6 seconds or about 1700 hours would be required to obtain one mole, 6×10^{23} molecules, of reaction product if one molecule is formed per quantum absorbed. Analytical procedures are available which may be employed on as little as 10^{-6} and 10^{-7} gram molecules. A light intensity of the above magnitude would produce enough reaction products to be analyzed in a matter of seconds, but the intensity would be too low for the synthetic chemist unless the reaction were of the chain type.

An idea of the energies involved is given by the following. At 4000 Å., 10^{17} quanta per second corresponds to 0.05 watt and at 2000 Å., to 0.10 watt. A filament lamp emits only 15% at most in the visible spectrum. A 10-watt bulb would emit roughly 0.05 watt in a range of wave lengths 10 Å. wide. However, this radiation goes in all directions, and usually not more than 1% could be utilized in a precise photochemical experiment. Therefore a 1000-watt bulb would be necessary, and the efficiency would be only about 0.005%. With high pressure mercury arcs the situation is just as bad or worse. Most of the energy input goes into heating the water flowing through the jacket, and the output in any single spectral line is very small, indeed. These considerations show how important it is to surround the light source completely with a reaction vessel (see page 99) and to use absorbing molecules which use a large range of wave lengths if a photochemical reaction is to be used where yield and expense are important.

Highly monochromatic light giving a total of more than 10^{14} to 10^{15} quanta per second is very difficult to obtain, particularly if the optical system is of the type desired for studies of mechanism. The beam for such investigations should be homogeneous and parallel, particularly if the rate of the reaction being studied is not directly proportional to the intensity. Thus relatively long exposures are necessary even if micromethods are used to determine the amount of reaction.

B. SELECTION ACCORDING TO PURPOSE OF WORK

The three types of sources will generally be different.

Absorption Spectra. For the study of absorption spectra a very high intensity is usually unnecessary, but the light should be continuous, *i.e.*, contain all wave lengths in the region under investigation, so that irregularities in the light source are not superimposed upon the absorption spectrum. Light sources for absorption spectra are discussed in detail in *Physical Methods of Organic Chemistry*.[7a]

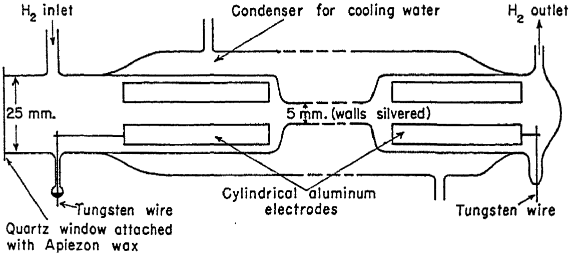
H_2 inlet
Condenser for cooling water
H_2 outlet
25 mm.
5 mm. (walls silvered)
Cylindrical aluminum electrodes
Tungsten wire
Tungsten wire
Quartz window attached with Apiezon wax

Fig. 1. A simple hydrogen discharge tube of over-all length from 40 to 60 cm.

An ordinary filament lamp may be used in the visible, *i.e.*, from about 4000 to 7000 Å. For the general region 1700 to 4000 Å. an uncondensed high potential discharge through hydrogen at low pressures is best. Lamps of this type are available commercially. A simple type which has been used by the author and can be made in the laboratory by a competent glass blower is shown in Figure 1. The hydrogen should be flowed continuously through this lamp in such a way that the hydrogen pressure is reasonably constant. The discharge should be bluish in color and the pressure regulated just below the highest at which a "striated" discharge is observed. A 1-kva transformer with a secondary voltage of 10,000 to 25,000 can be used without secondary condenser. The intensity will be adequate for obtaining spectra with medium-sized spectrographs.

[7a] Weissberger, ed., *Physical Methods of Organic Chemistry*, Interscience, New York.

Reaction Mechanisms. For the study of reaction mechanisms highly monochromatic radiation is usually desirable. Absorption coefficients, quantum yields, and even the nature of the products may depend on wave length. Monochromatic radiation is essential to avoid introducing unknown variables in the interpretation.

High Yields. A high intensity is essential for obtaining high yields unless the reaction is of the chain type. Two types of information are necessary before proceeding to use a high intensity of polychromatic light: (*1*) the variation of the nature of the products with wave length and with intensity; and (*2*) the effect of temperature on the yield and on the nature of the products.

(*1*) For certain reactions the yield is independent of wave length, but for others a marked variation is noted. If there is a variation, it is usually of such a character that for a given amount of absorption the yield increases with decreasing wave length. However, at least a preliminary investigation of the absorption spectra of the reactants and of the effect of wave length on the yield is advisable before proceeding to use polychromatic light of high intensity.

In some instances the character of the reaction changes with wave length. To cite a simple example, biacetyl is formed from acetone in appreciable quantities at wave lengths[8] 2500 to 3100 Å., but none seems to be formed[9] at 1850.

Another effect may be important. The products of a reaction may themselves undergo photochemical change if they absorb light. To use the same example, biacetyl decomposes photochemically at 3100 Å. and particularly[10,11] at 3660 Å. Thus irradiation of acetone will cause biacetyl to build up only to a low partial pressure such that its rate of formation becomes equal to its rate of disappearance. With polychromatic light containing both 3100 and 3660 Å. (the latter is not absorbed by acetone) the steady-state value of biacetyl would be expected to be lower than with monochromatic radiation of wave length 3100 Å. In this case the yield of biacetyl will be increased in a flow or circulating system in which biacetyl is removed rapidly from the illuminated zone.

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[8] *Cf.* Davis, *Chem. Revs.*, **40**, 201 (1947), for a review.

[9] Howe and Noyes, *J. Am. Chem. Soc.*, **58**, 1404 (1936).

[10] Anderson and Rollefson, *J. Am. Chem. Soc.*, **63**, 816 (1941).

[11] Roof and Blacet, *J. Am. Chem. Soc.*, **63**, 1126 (1941). See also Norrish and Griffiths, *J. Chem. Soc.*, **1928**, 2828.

(*2*) It should be kept in mind also that polychromatic light may contain a lot of infrared and hence may cause a considerable increase in temperature of the reacting system unless precautions are taken. Even when infrared is absent an intense light source may lead to a considerable rise in temperature, especially if the reaction is exothermic. This may change the character of the reaction. To use the same example, little or no biacetyl is formed from acetone at temperatures over 60°C.

C. SELECTION ACCORDING TO NATURE OF REACTANTS

Monatomic Gases. White light, *i.e.*, light containing all wave lengths over a broad region, contains radiation which will be absorbed by monatomic gases, but the fraction absorbed will be exceedingly small. Thus the fraction of the energy input into such a light source which would be utilized is so infinitesimal as to make the cost of any product made in this way very high unless the reaction is of the chain type.

Practically speaking the only useful light sources for the monatomic vapors mentioned on page 85 are arcs or discharges in the vapors themselves. Thus, *mercury vapor* lamps emit lines absorbed by mercury vapor, *cadmium vapor* lamps emit lines absorbed by cadmium vapor, etc. Commercial lamps (Hanovia Chemical Co.) are available which give a high intensity of the 2537.5 Å. line of mercury, thus permitting the use of mercury sensitized reactions.[12] The vapor pressure of mercury is high enough even at 0°C. to give a high absorption of this line in a short path length. The practical use of mercury-sensitized reactions is, therefore, feasible. For the *other gases and vapors* listed on page 85 special lamps must be constructed, but except for *xenon* the vapor pressures are so low that reactions may only be carried out above room temperature. Xenon has one serious drawback in that the wave lengths involved are not transmitted by either glass or quartz.

One fact concerning these light sources must be stressed. The light emitted by the gas or vapor is absorbed strongly by the same gas or vapor and hence will be completely absorbed within the light source unless care is taken. This absorption may be avoided to some extent by operating low pressure mercury arc lamps under water, but a high intensity of 2537.5 Å. light is obtained only in a discharge tube filled with mercury vapor and a foreign gas, such as argon, and operated at high potential.[12] This is the type of lamp sold commercially. Sources of *cadmium*,[13] *zinc*,[14] and *xenon*[15] radiation have been described by various authors.

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[12] *Cf.* Noyes and Leighton, *The Photochemistry of Gases.* Reinhold, New York, 1941, p. 38.

Diatomic Molecules. To produce photochemical effects following absorption by *diatomic molecules*, one is interested primarily in those wave lengths which cause dissociation, *i.e.*, shorter than 4785 for chlorine, 5107 for bromine, and 4989 for iodine. These three wave lengths all lie in the blue-green part of the visible spectrum. Thus, any source of white light which contains a high intensity in the blue and violet will dissociate these molecules. Diffuse daylight is adequate to cause certain reactions, particularly chlorinations, to proceed, but if greater reaction rates are desired, direct sunlight or ordinary Mazda lamps may be used.

Mercury arcs also contain light which is able to dissociate *halogen* molecules. Three lines particularly are effective: 4370, 4050, and 3660. Any mercury arc will give sufficient intensity to start chlorinations, but brominations and particularly iodinations are so slow that high pressure high intensity arcs of the type H-3, H-4, and AH-6 (see page 95) are desirable. Carbon arc lamps also give a high intensity in the visible spectrum and may be used. Almost any light source is good enough to cause reactions by the halogens. Since visible light is required, ordinary glass apparatus may be used.

Mercury arc lamps of the ordinary therapeutic type do give some light absorbed by *oxygen* as evidenced by the odor of ozone which is usually found around such arcs. However, the intensity of the light absorbed by oxygen is so low as to make their use impracticable. A spark between aluminum electrodes may also be used, but since oxygen is present in the air, much of the radiation which might be desired in the reacting system is absorbed if the air path is over one or two centimeters. Possibly the best source of radiation for oxygen is a hydrogen discharge tube (see Fig. 1), but the window of this discharge tube should be in contact with the window of the reaction vessel, or, better yet, one window may be used in common by the discharge tube and the reaction vessel.

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[13] Bates and Taylor, *J. Am. Chem. Soc.*, **50**, 771 (1928). Steacie and LeRoy, *J. Chem. Phys.*, **12**, 34 (1944). Bender, *Phys. Rev.*, **36**, 1535 (1930).

[14] Hoffman and Daniels, *J. Am. Chem. Soc.*, **54**, 4226 (1932). Habeeb, LeRoy, and Steacie, *J. Chem. Phys.*, **10**, 261 (1942).

[15] Groth, *Z. Elektrochem.*, **42**, 533 (1936); *Z. physik. Chem.*, **B37**, 307 (1937).

Carbon monoxide absorbs only at very short wave lengths, and the only light source convenient for reactions involving these molecules is a xenon lamp.[16] Reactions involving carbon monoxide, while of great theoretical interest, may be of little value to the synthetic chemist.

Polyatomic Molecules. The 2780 Å. line of mercury and all shorter wave lengths provide energy enough to break the *carbon-hydrogen bond.* Lines at longer wave length probably do not. The 3130 Å. line and perhaps the 3380 Å. line are adequate to break most *carbon-carbon single bonds.* Of course such bonds do not necessarily dissociate just because enough energy is provided.

2. Light Sources for Study of Reaction Mechanism

A. MERCURY ARCS

Since monochromatic light is desired in the study of the mechanism of photochemical reactions, the research worker is confronted with a very serious problem. Various forms of mercury arc constitute the only convenient sources for obtaining approximately monochromatic light because the lines of the mercury spectrum are separated sufficiently to permit either the use of color filters or the use of a monochromator. The following lines of the mercury spectrum are obtained with low voltage mercury arcs: 1849, 1942, 2537, 2652–54, 2804, 3021, 3126–31, 3650–63, 4046, 4358, 5461, 5770–91. Under some conditions light sources may be obtained which give very high intensities of one of these lines with the almost complete exclusion of most of the others. This is particularly true of the line at 2537 Å. (see page 92).

The 1849 line is not well transmitted by fused quartz and in any case is difficult to obtain pure. 1942, 2652–54, 2804, 3021, and 5770–91 are generally weaker than the others in most arcs. The lines at 2537, 3126–31, and 3650–63 are the most useful for photochemical work.

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[16] Groth, *Z. physik. Chem.*, **B37**, 315 (1937).

A variety of high pressure mercury arcs have been described in the literature,[17] and some are sold commercially. With a large monochromator using quartz lenses of about 10 cm. in diameter and 10 cm. focal length and a prism of quartz roughly 10 cm. on edge with an equilateral triangle as a base, it is possible to obtain as much as 10^{17} quanta per second through the exit slit. The optical characteristics will be such that the emergent beam will not be strictly parallel and would be difficult to focus down a long reaction tube without danger of scattering from the walls. Nevertheless, this type of light source and monochromator may be extremely useful in photochemical studies, particularly if one or the other of the following mercury lines can be used: 3130, 3660, 4060, 4370, and 5461.

Some of the high pressure mercury arcs, particularly the AH-6 manufactured by the General Electric Company, operate at such high pressures that the spectrum lines are very broad and diffuse. Even with a monochromator it is impossible to obtain a range of wave lengths less than 50 Å. unless the slits are so narrow that the intensity is reduced below 10^{17} quanta per second.

Low pressure mercury arcs of the type sold for therapeutic use are usually manufactured with quartz tubes one or more centimeters in diameter and perhaps 5 or 10 cm. in length. The emission of these lamps in terms of quanta per unit area per second is so small as to render them relatively useless for quantitative photochemical work. The best type of lamp from the standpoint of steadiness and reasonably high intensity is either the Uviarc or several types of capillary arc operating at pressures of only a few atmospheres.[13]

Quartz prism monochromators are available commercially, although the transmission through most of them is too low for photochemical work. Special ones have been designed and made, but the design must be carefully planned to avoid excessive light scattering and to insure sufficient intensity.

For use with monochromators a mercury arc in capillary tubing not much greater in diameter than the slit width is advisable. Most of these operate at quite high pressure, and the emission lines are broad. Examples are the H-3, H-4, AH-6, and Uviarcs manufactured by the General Electric Company and Hanovia Chemical Company. The

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[17] *Cf.* Noyes and Leighton, *The Photochemistry of Gases*, Reinhold, New York, 1941, Chapter II. See also Hoffman and Daniels, *J. Am. Chem. Soc.*, **54**, 4226 (1932).

TABLE III
Filters for the Mercury Arc Lines[18]

Mercury line desired, Å.	Filter	Remarks
5770–90	$CuSO_4 \cdot 5H_2O$, 11.1 g./100 cc. H_2O, 1 cm. layer, plus $K_2Cr_2O_7$, sat. soln., 2.5 cm. layer	Transmits 36% at 5770, and some at 5460. May be supplemented with a 3 to 4 mm. layer of Corning glass 344
5460	$CuCl_2 \cdot 2H_2O$, 4.57 g./100 cc. ethyl alcohol 1 cm. layer, plus $CoCl_2 \cdot 6H_2O$, 1.4 g./100 cc. acetone, 5 mm. layer	Transmits only 6.5% at 5460
4358	$KMnO_4$, 0.84 g./l. H_2O, 1 cm. layer plus $CuCl_2 \cdot 2H_2O$, 37.5 g./100 cc. H_2O, 5 mm. layer	Transmits 12% at 4358, very little 4047–78
4047–78	$CuSO_4 \cdot 5H_2O$, 0.44 g./100 cc. 2.7 M NH_4OH, 10 cm. layer, plus I_2, 0.75 g./100 cc. CCl_4, 1 cm. layer, and quinine hydrochloride, 1 g./100 cc. H_2O, 2 cm. layer	Renew iodine and quinine solutions frequently
3660	$Cu(NO_3)_2 \cdot 6H_2O$, 16.7 g./100 cc. H_2O, 5 mm. layer, plus Wratten No. 18 filter	Transmits 10% at 3660, very little at 3550 or 4047–78
3125–31	$NiSO_4 \cdot 6H_2O$, 46 g., plus $CoSO_4 \cdot 7H_2O$, 14 g., in 100 cc. H_2O, 3 cm. layer, plus potassium acid phthalate, 5 g./l. H_2O, 1 cm. layer	The $NiSO_4$ and $CoSO_4$ must be very pure, especially free from iron. Renew phthalate frequently. Transmits 80% at 3130, 3% at 3342, almost none at 3020
3125–31[19]	0.178 M $NiCl_2$, 5 cm., 0.0005 M K_2CrO_4, 5 cm., 0.0245 M $KHC_8H_4O_4$, 1 cm., Red Purple Corex Glass (Corning No. 9863), 5 mm.	About 25% of this group of lines is transmitted and no radiation outside the limits 3100–3300 Å. is transmitted
2652–2804	$NiSO_4 \cdot 6H_2O$, 100 g./100 cc. H_2O, 1 cm. layer, plus $KMnO_4$, 0.84 g./l. H_2O, 5 mm. layer	Transmits mainly 2654, some 2804, and ∽ 2% of 4358
2537	I_2, 0.108 g., plus KI, 0.155 g. in 1 l. H_2O, 1 cm. layer, plus $NiSO_4 + CoSO_4$ layer as for 3125–31 (above) if desired	Transmits ∽ 20% at 2537, very little at 2654 Å.
2320–2804	Gaseous Br_2, 0.0046 M, plus gaseous Cl_2, 0.176 M, in 6 mm. layer. Partial pressures, at 40°C., Br_2 0.12 atm., Cl_2 4.5 atm.	Transmits 18% at 2320, 27% at 2537, 16% at 2654, 12% at 2804, ∽ 1% at 3020–3660, and 13% at 4047

Note: Commercial filters made by *Corning Glass Co.* and *Farrand Optical Co.* are useful for many mercury lines.

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[18] *Cf.* Noyes and Leighton, *loc. cit.*, p. 69. Bowen, *The Chemical Aspects of Light*, Clarendon, Oxford, 1946, p. 276, gives other various useful filters for mercury lines.

[19] Hunt and Davis, *J. Am. Chem. Soc.*, **69**, 1415 (1947).

H-3 and H-4 arcs have glass outer envelopes which must be removed for use below 3500 Å. When outer envelopes are removed, the useful lives of these arcs are short. Moreover, they operate at such pressures as to be dangerous. Personnel must be protected both from the radiation and from possible flying fragments. The AH-6 arc has the advantage of very high intensity, but the emission lines are broader than from any of the others, and the intensity is not so constant. The AH-6 arc must be water-cooled and will invariably explode if the water flow stops.

B. FILTERS FOR USE WITH MERCURY ARCS

Several color filters for use with mercury arcs have been described While many of them are reasonably satisfactory, if a high "purity" is desired, the intensity will always be lowered appreciably. A few of these filters are as follows.

Various glass filters, particularly for the mercury lines in the visible spectrum, may be purchased from several companies.

C. SPARKS AND OTHER SOURCES

Light sources other than the mercury arc have been used for quantitative photochemical work. Thus sparks between aluminum electrodes are particularly useful in the region between 1800 and 2000 Å., but the aluminum vaporizes, and consequently the distance between the electrodes changes quite rapidly, unless the spark is between two aluminum discs with beveled edges rotating slowly at right angles to each other.[20] The discs should be 5 to 10 cm. in diameter and rotate one to five times per minute. If the power input is about 1000 watts operating on a secondary voltage of 15,000 to 20,000 with a condenser in parallel, intensities up to 10^{13} and 10^{14} quanta per second can be obtained. Zinc sparks are also very useful for wave lengths somewhat greater than 2000 Å.

Other sources are much less commonly used for quantitative photochemical work. Filament lamps with color filters or with prism monochromators may be used to give a band of wave lengths provided that the reaction being studied does not have a yield highly dependent on wave length. If the reacting materials have monochromatic absorption spectra continuous sources may be used. *Sodium vapor*

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[20] Wiig and Kistiakowsky, *J. Am. Chem. Soc.*, 54, 1806 (1932).

lamps, sold commercially, may be used to give a high intensity of the D lines. Most other sources give too low intensities to be of general use.

3. Light Sources for Large Yields

A. SUNLIGHT

Even if it is necessary to use color filters to obtain approximately monochromatic light, the intensity of bright summer sunlight exceeds anything which can be reasonably obtained in the laboratory. However, the range of wave lengths is somewhat limited, and the heat absorbed by the system may produce undesirable effects unless the light is suitably filtered. Even in the middle of summer sunlight can rarely be observed to extend below about 2900 Å., and intensities at the shorter wave lengths are quite small. Since photochemical reactions rarely occur in the infrared, sunlight is mainly useful in the range from 3500 to 6000 Å.

Much, but not all, of the infrared may be removed by water. A flask filled with water may even be used to focus sunlight or light from filament lamps (see below), but this will not prevent increase in temperature so that thermostating may sometimes be necessary. A 0.2 M $CuCl_2$ solution is effective in cutting out nearly all radiation of wave length[21] greater than 6000 Å. A 2-cm. layer of 0.2 M $CuCl_2$ and 1.25 M $CaCl_2$ transmits mainly from 4600 to 6000 Å. Lowering the concentration of $CuCl_2$ to 0.43 M extends the transmission to about 4000 Å.

B. FILAMENT LAMPS

For those reacting systems which absorb in the visible and the near ultraviolet, 500- or 1000-watt Mazda lamps can be extremely useful, but it should be remembered that these give out considerable amounts of infrared, and that consequently the reaction vessel should be thermostated as well as shielded by a layer of water from the light source. Since all of the halogens absorb in the visible, Mazda lamps offer by all odds the most convenient source of radiation for halogenations even though the percentage of the energy appearing as absorbable visible radiation is relatively small.

[21] Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 72 (1921).

C. MERCURY ARCS

Other light sources, particularly the mercury arc, may be used in this connection also. If monochromatic radiation and a refined optical system are unnecessary, reaction vessels may be built around these arcs in order to take complete advantage of the emitted radiation.[22] Under such conditions 10^{20} or more quanta per second are available, and reactions may be made to yield grams of products in a matter of seconds, even if the quantum yield is low. Arcs of this type are manufactured and in some instances, used commercially.

D. OTHER LIGHT SOURCES

Another source of radiation which should be mentioned is the ordinary carbon arc which may be made to have a spectral distribution roughly equivalent to that of sunlight, particularly if the carbons are impregnated with the salts of certain heavy metals.[23] It should be remembered, however, that carbonlike arcs, high-pressure arcs, and Mazda lamps give out large amounts of heat and that if the reaction involves thermolabile compounds due care must be taken to dissipate the heat.

For radiation of high intensity but far from monochromatic, the hydrogen discharge[24] may be used. In fact the range covered is from about 4000 Å. down to the limit of transmission of CaF_2 or LiF, *i.e.*, about 1200 Å. The *xenon lamp* gives two very intense lines at 1295 and 1470 Å. and may be useful for certain reactions in the far ultraviolet.[15]

IV. CONCEPT OF QUANTUM YIELD

1. Single-Step and Multiple-Step Reactions

The Einstein Law of Photochemical Equivalence states that one molecule reacts per quantum absorbed. In practice all types of reactions are known, from those in which only a very small fraction of one molecule goes into final products per quantum absorbed to chain reactions in which a million or more molecules may react per quantum absorbed.

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[22] Bates and Taylor, *J. Am. Chem. Soc.*, **49**, 2438 (1927).

[23] Carbons of this type impregnated with salts of several heavy metals may be purchased under several names, such as "Daylight" or "Sunlight." When used in an ordinary carbon arc lamp the spectrum extends to about 2500 Å., but it is quite weak below 3000 Å. In a rough way the light from such an arc resembles sunlight.

[24] Hydrogen discharge tubes may operate either on low [*cf.* Allen and Franklin, *J. Optical Soc. Am.*, **29**, 453 (1939)] or high voltage [*cf.* Almasy, *Helv. Chim. Acta,* **10**, 471 (1937)]. See Noyes and Leighton, *The Photochemistry of Gases*, Reinhold, New York, 1941, pp. 29 *et seq.*

There is no point in discussing the philosophical meaning of a quantum at this time. A quantum of radiant energy is $h\nu$ ergs where h is Planck's constant (6.61×10^{-27} erg seconds) and ν is the frequency. The frequency is equal to the speed of light (3.00×10^{10} cm. per sec.) divided by the wave length in centimeters. Keeping in mind that one angstrom unit is 10^{-8} cm., the value of a quantum is seen to be $1.983 \times 10^{-8}/\lambda$ ergs where λ is in angstrom units. A number of quanta equal to Avogadro's number is often called an einstein, *i.e.*, $6.02 \times 10^{23} \times 1.98 \times 10^{-8}/\lambda$ ergs $= 1.19 \times 10^{16}/\lambda$ ergs. Thus an einstein of red light (6000 Å.) corresponds to 1.983×10^{12} ergs $= 1.983 \times 10^{5}$ joules $= 47{,}400$ cal. At 2000 Å. the corresponding figures are 5.95×10^{5} joules or 142,000 cal. The energy of the quantum absorbed must be equal to or greater than the energy required to produce whatever effect is required in the absorbing molecule, *i.e.*, either dissociation or activation.

The primary effect of the radiation, as has been pointed out on page 82, is to produce either energy-rich molecules or fragments of molecules, usually atoms or free radicals. The energy-rich molecules may, probably rarely, rearrange eventually or immediately into final products, or they may eventually dissociate into free radicals or atoms. In some instances they may collide with other molecules and transfer all or part of their energy to them. In such cases they are said to perform the role of *sensitizers.* The best example of the latter is found in the effect of mercury atoms which absorb 2537 Å. radiation and induce a large variety of chemical reactions. The mercury atoms do not disappear permanently. The role of chlorophyll in photosynthesis of plants, while considerably more complex than that of mercury atoms, is essentially that of a photosensitizer since it is not finally transformed.

If the light produces atoms or radicals, these may undergo further reactions either with themselves or with other molecules in the system. If recombination reactions predominate over all others, the net quantum yield may be exceedingly small. If, on the other hand, these atoms or radicals react with other molecules to form new atoms or new radicals, a chain of events may be started which may continue until it comes to an accidental end. In some instances as many as 10^6 molecules may react per quantum absorbed. Many of the reactions involving chlorine are of the chain type whereas most of the reactions involving bromine, although they may be of the same type, are of such a character that recombination is important, the chains are short, and the yields are relatively low.

2. Radiation Standards

The precise experimental determination of quantum yield need not concern us in detail in this chapter. In order to determine this quantity it is necessary to measure in absolute units the amount of light absorbed by the reaction system per unit time and to determine simultaneously the number of molecules of product or the number of molecules disappearing per unit time. Thus in the reaction:

$$CH_3COCH_3 \rightarrow CO + C_2H_6 \tag{16}$$

one may speak either of the quantum yield of carbon monoxide formation, the quantum yield of ethane formation, or the quantum yield of acetone disappearance. Of course, if this chemical equation represents the only reaction taking place, the knowledge of one of the three quantum yields immediately gives the value of the other two since the three yields are identical. However, if reaction (16) is accompanied by the reaction:

$$2\ CH_3COCH_3 \rightarrow (COCH_3)_2 + C_2H_6 \tag{17}$$

the quantum yield of ethane formation will no longer be equal to that of acetone appearance. Thus it is essential in speaking of quantum yields to refer to the specific compound which is being determined analytically and for which the yield is given.

There is only one absolute source of radiant energy: a true "black body." This would consist of a hollow vessel inside of which the temperature is uniform and the radiation is in equilibrium with the walls. If one wall of such a vessel is perforated by a pinhole which allows a small amount of radiation to escape, it may be assumed that the loss of this radiation does not disturb the equilibrium inside the vessel. Under such conditions the radiation coming out through the pinhole obeys Stefan's law:

$$I = aT^4 \tag{18}$$

where the constant a has the value 5.672×10^{-5} erg cm.$^{-2}$ deg.$^{-4}$ sec.$^{-1}$. The complete theory of black body radiation enables the constant a to be expressed in terms of fundamental constants of nature, all of which can be evaluated by independent methods with a high accuracy.[25] Therefore the radiation coming out of the pinhole may be taken as known with high precision if the area of the pinhole and the temperature can be determined precisely.

There are some difficulties in using this type of "black body" as a standard of measurements for radiant energy. In the first place the light coming out of the pinhole contains all wave lengths from the far infrared to the extreme ultraviolet, although the extremes will have low intensities. Any measuring instrument which is to be used must, therefore, respond with equal effectiveness to a given number of ergs per square centimeter per second regardless of the wave length or frequency. Few instruments of this type exist, although it is possible to take a single- or multiple-junction thermopile and coat the junctions with platinum or carbon black so that the temperature rise very closely measures total radiation independent of wave length.[26] If such a thermopile is used (some can be purchased from various companies, and it is possible also to make them oneself with a little care) it can be used with a galvanometer as a direct reading instrument which can be calibrated by means of a black body and Stefan's law.

To avoid the difficulty of establishing a true black body, something which is difficult in actual practice, one can purchase *standard lamps* from the Bureau of Standards for which the total emission in a specified direction, indicated by markings on the glass, has been carefully determined as a function of the current through the lamp. These lamps furnish convenient standards for calibrating thermopiles.

3. Measurement of Intensity

A. THERMOPILES

It should be remembered that thermopiles are calibrated with radiation which lies largely in the infrared whereas they are to be used for photochemical work mainly with visible or ultraviolet radiation. One must determine, therefore, that the response of the thermopile is dependent only on energy per unit area per second and is strictly independent of wave length. A complete test of this type is not easy, but it is done with adequate care in most cases by varying the current through the *standard lamp* as indicated on the Bureau of Standards certificate and by proving that the response of the thermopile–galvanometer system is linear with intensity. Since the wave length distribution changes with temperature of the filament—shorter wave lengths being a larger fraction of the total at high temperatures—a linear response usually is a sufficient guarantee that the system may be used for all wave lengths apt to be used photochemically.[27]

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[25] Birge, *Rev. Modern Phys.*, 13, 233 (1941).

[26] *Cf.* Noyes and Leighton, *loc. cit.*, p. 79.

B. PHOTOELECTRIC CELLS

Photoelectric cells are sometimes used to measure light intensities, but the response of a photoelectric cell is by no means independent of wave length. Therefore they cannot be calibrated either directly or indirectly by Stefan's law. However, if a thermopile has been properly calibrated and has been shown to have a response independent of wave length, and if a source of monochromatic radiation is then used, the readings of the thermopile–galvanometer circuit may be compared with the readings of the photoelectric cell circuit. Thereafter the photoelectric cell may be used for that one wave length only. It should always be kept in mind, however, that frequent recalibration with such a system is essential to avoid errors.

C. CHEMICAL ACTINOMETERS

In many instances it is more convenient to use a *chemical actinometer* than any other device for measuring intensities. These have several advantages. Most light sources show intensity variations both with time and over the area of any beam passing through a reaction vessel. Either thermopiles or photoelectric cells must be used in such a way that the integration over time, intensity, and area is obtained so that the total number of quanta incident on the reaction vessel has been measured. This means moving the light-measuring device around throughout the cross section of the beam in a systematic manner so that the total light can be determined and also means plotting the intensity as a function of time and obtaining the area under the curve. Both of these procedures are laborious and may introduce errors. Chemical actinometers of the proper type, however, integrate over time and intensity and, if used in cells large enough to intercept the entire light beam, will also integrate over the area of the beam.

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[27] Standard lamps obtained from the U. S. Bureau of Standards are accompanied by a calibration certificate and detailed instructions for use.

The characteristics of a chemical actinometer must be the following: (*a*) insensitivity of yield to wave length variations in the region of wave lengths to be studied; (*b*) small variation of quantum yield with temperature; (*c*) rate of reaction proportional to the first power of the intensity; and (*d*) definiteness of the chemical reaction, *i.e.*, there must not be troublesome and variable side reactions.

Few photochemical systems meet the requirements for good actinometry. The best ones are: (*a*) uranyl oxlate; (*b*) gaseous hydrogen bromide; (*c*) gaseous hydrogen iodide; (*d*) gaseous oxygen; and (*e*) gaseous carbon dioxide. Most of the others described in the literature are subject to one objection or another. Gaseous acetone at temperatures over 100°C. is satisfactory for certain purposes.

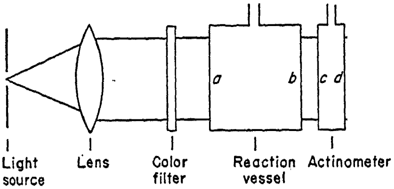

Fig. 2. Chemical actinometer.

In using an actinometer the following *precautions* must be taken: (*1*) Corrections will have to made for light reflected, absorbed, or scattered by the windows of the reaction vessel and of the actinometer cell. In case the radiation is not strictly monochromatic it may be difficult to make these corrections, although they may usually be made empirically with adequate precision for any but the most accurate work. (*2*) All wave lengths absorbed by the reacting system must also be absorbed practically completely (over 90 and preferably over 99%) by the actinometer. If this is not true, the apparent value of the light absorbed as measured by the actinometer will not correspond to the true value of the light absorbed by the reacting system. (*3*) While the actinometer will integrate intensity over time and area reasonably accurately, the same will not necessarily be true if the wave length distribution of the light source–filter combination changes with time. This error is particularly serious if, as often happens, the quantum yield of the reacting system varies with wave length. Indeed, if there is such a variation, the only significant values are ones obtained with highly monochromatic light, something very difficult to obtain in sufficient intensity for this type of study. (4) The light beam must be focused in such a way that all parts of it not absorbed by the reacting system enter the actinometer. If the beam is not strictly parallel as indicated in Figure 2, the actinometer cell must be large enough so that the entire emergent beam enters, and none hits the walls before it is absorbed. Often actinometer cells in the form of truncated cones have been used for this reason. So many geometrical arrangements are possible in this connection that it is useless to describe all of them in detail, and this point is emphasized merely so that the experimenter will keep it firmly in mind.

Uranyl Oxalate Actinometer. The uranyl oxalate actinometer utilizes the reaction:

$$H_2C_2O_4 \rightarrow H_2O + CO_2 + CO$$

It must be used with care. Its main characteristics are described as follows:

Concentration of UO_2SO_4, 0.01 *M*
Concentration of $H_2C_2O_4$, 0.05 *M*
Useful range, about 4400 Å. to about 2000 Å.

The actinometer cell must be kept within two or three degrees of 25°C. If for any reason the reacting system is being studied at higher temperatures, due care must be taken to prevent the actinometer from being warmed by radiation.

For most accurate results a small stirrer should be introduced into the actinometer cell.

The oxalate may be titrated with $KMnO_4$ solutions.

Since the light intensity measurement is based on the difference between two titrations, one with the reaction cell empty and the other with the cell filled with the reacting mixture, the volume of the actinometer cell should be kept as small as possible consistent with nearly complete absorption. The thickness of cell necessary for complete absorption is less at short wave lengths than at long. For 99% absorption, 15 to 20 cm. would be required at 4358 Å. but only 0.5 cm. would be necessary at 3130 Å. Since this actinometer is best adapted to use at 3660 Å. and below, the thickness may be 12 cm. or less.

It will be noted from Table IV that variations with wave length are relatively minor over quite a long range. If equipment is available for using mercury arc lamps and isolating the single lines referred to in the table, the exact values should be used. If, however, polychromatic light is used, *i.e.*, either several lines of the mercury arc or some other light source not giving well-isolated lines, a quantum yield of 0.55 may be used with sufficient accuracy for most purposes over the entire range from 2000 to 4000 Å.

TABLE IV

Uranyl Oxalate Actinometer

Quantum Yields in Terms of Molecules of C_2O_4 Disappearing per Quantum Absorbed[28]

Wave length, Å.	Quantum yield	Wave length, Å.	Quantum yield
4350	0.58	3020	0.57
4050	0.56	2780	0.58
3660	0.49	2650	0.58
3350	0.53	2540	0.64–0.60
3130	0.56	2080	0.47–0.50

To illustrate the way in which the actinometer can be used to determine the number of quanta absorbed by the reacting system, let us consider a typical example.[29]

Step 1. The reaction vessel is empty, *i.e.*, it is evacuated if one is dealing with a gas reaction, or it is filled with air or with carefully purified solvent if one is dealing with a liquid phase reaction. The actinometer cell is filled with the uranyl sulfate – oxalic acid solution, and the light is turned on for the time t_1. Let N_1 be the number of equivalents of $KMnO_4$ solution used for the titration with the reaction vessel empty and no light and N_1' be the number of equivalents required after irradiation for time t_1.

Step 2. Fill the reaction vessel with the reaction mixture and refill the actinometer. Expose for the time t_2. Let N_2 be the number of equivalents of $KMnO_4$ solution required for titration of the actinometer solution after this exposure. The volume of actinometer solution should be carefully measured and the same volume used each time.

Step 3. Repeat step 1 both as a check on the titrations and to ascertain whether or not the light source has remained constant. Let N_3 and N_3' be the titrations in step 3 corresponding to N_1 and N'_1 in step 1, the time of exposure being t_3.

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[28] Forbes and Leighton, *J. Am. Chem. Soc.*, **52**, 3139 (1930). Forbes, Kistiakowsky, and Heidt, have described an apparatus for determining gas quantum yields by actinometry, *J. Am. Chem. Soc.*, **54**, 960 (1932).

[29] *Cf.* Noyes and Leighton, *loc. cit.*, p. 84.

During some reactions solid *deposits* form on the walls of the vessel, thus vitiating measurements of light intensity completely. No precise correction can be made for this effect. If the amount of deposit is small, a series of measurements of quantum yield may permit extrapolation back to zero time, *i.e.*, to the state with clean windows. In some instances the deposit may be kept away from the windows by warming them slightly above the temperature of the rest of the vessel.

Certain light sources undergo a gradual and *regular change in intensity* with use. This is particularly true for certain types of mercury arc since the transmission of the quartz gradually decreases. The results of steps 1 and 3 may not check, but the arithmetical mean may be used as an adequate approximation of the value the blank would have had during step 2. However, if steps 1 and 3 do not check, a number of determinations of the blank should be made to ascertain definitely that the change in intensity emitted by the lamp is regular and not sporadic.

Other light sources undergo unsystematic and *random fluctuations in intensity*, particularly if the voltage of the line used to operate them is not steady. If this is the case, the results are not reliable. Various devices have been used to make corrections for this type of variation, but none is really satisfactory. A photoelectric cell may be placed in such a way as to intercept part of the light beam, or it may be interchanged with the actinometer. Determination of the area under a curve of galvanometer deflection against time gives a measure of important fluctuations in the integrated intensity, and all results can be corrected back to a standard condition provided that the light is monochromatic.[29,30]

As a general rule steps 1 and 3 should check to better than 10% or the results should be discarded.

$(N_1 + N_3)/2$ = average number of equivalents of $C_2O_4^{--}$ in the actinometer cell = $\bar{N}_1$.

$(\bar{N}_1 - N'_1)/t_1$ = number of equivalents of $C_2O_4^{--}$ disappearing per unit time due to irradiation of the actinometer through the empty reaction vessel during step 1. (Note: The light must be intense enough and the time of exposure long enough so that $(\bar{N}_1 - N'_1)$ has the necessary accuracy.

$(\bar{N}_1 - N'_3)/t_3$ = corresponding quantity from step 3. This should check with the preceding.

Put $[(\bar{N}_1 - N'_1)/t_1 + (\bar{N}_1 - N'_3)/t_3]/4 = n_1$ = average number of moles of $C_2O_4^{--}$ disappearing per unit time during irradiation of the actinometer through the empty reaction vessel.

Similarly, $n_2 = (\bar{N}_1 - N_2)/2t_2$ = average number of moles of $C_2O_4^{--}$ disappearing per unit time when the actinometer is irradiated through the filled reaction vessel (step 2).

$(n_1 - n_2)$ would be equal to the number of gram molecules of $C_2O_4^{--}$ disappearing due to radiation absorbed by the reacting substances *providing* there is no loss of intensity in passing through the windows *b* and *c* (Fig. 2). This will never be true.

$(n_1 - n_2)/n_1 = F$ is the fraction of the light entering the reaction system through window *a* which is absorbed by the reacting substances to a first

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[30] Leighton and Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).

approximation. This would be rigorously true if: (a) the light is monochromatic; and (b) if none of the light reflected by the windows entered the reaction vessel or the actinometer. The second condition is, of course, not met. A rigorous treatment can be made if the light beam is parallel and monochromatic.[31] For practical work the procedure given is adequate for determining a quantum yield within 20%.

Step 4. Fill both the reaction vessel and the actinometer cell with the actinometer solution. Let N_1'' be the number of equivalents of $C_2O_4^{--}$ obtained in the blank with no light on in the reaction vessel and $\bar{N}_1''$ the same for the actinometer cell. $\bar{N}_1''$ should check with N_1, step 1, and with N_3, step 3. Now expose for a definite length of time and let N_2'' be the number of equivalents of $C_2O_4^{--}$ remaining in the reaction vessel and $\bar{N}_2''$ the number of equivalents after exposure in the actinometer cell.

$(N_1'' - N_2'')/2t_4$ = number of moles of $C_2O_4^{--}$ disappearing per unit time in the reaction vessel $= n_3$.

$(\bar{N}_1'' - \bar{N}_2'')/2t_4$ = number of moles of $C_2O_4^{--}$ disappearing per unit time in the actinometer vessel $= n_4$.

The same care to obtain reproducibility should be made with n_3 and n_4 as with n_1 and n_2.

$(n_1 - n_4)/n_1 = F'$, the fraction of light absorbed by the actinometer solution in the reaction vessel. If F is very nearly the same as F', corrections for multiple reflections may be neglected in what follows. Generally $F' \gg F$, in which case the calculations are only approximate, but in the most unfavorable case the error will not exceed 20%. If $F' = 1$ (*i.e.*, absorption by the actinometer solution in the reaction vessel is complete):

$$n_3 \times 6.02 \times 10^{23}/\Phi \doteq \text{number of quanta entering the reaction vessel} = I_1 \tag{19}$$

If $F' \neq 1$:

$$I_1 = (1/F')(n_3 \times 6.02 \times 10^{23}/\Phi) \tag{20}$$

where Φ is the number of molecules of actinometer solution reacting per quantum absorbed. If A is the number of molecules of the reacting system reacting per unit time (step 2), the quantum yield of the reaction is $A/I_1 \cdot 1/F$. The quantity A may be determined by any analytical procedure applicable to the system in question.

It must be repeated that actinometry will give correct results only if the actinometer solution absorbs all wave lengths in the beam which are absorbed by the reaction system. With care, however, actinometers give quantum yields as accurate as the quantum yields of the actinometers themselves are known.

Other Actinometers. The *gaseous hydrogen bromide actinometer*[32] is useful in the general spectrum region from about 1800 Å. to about 2500 Å., *i.e.*, toward the short wave limit of transmission of quartz. The hydrogen bromide pressure should be 5 to 10 cm. of mercury, and the actinometer cell must be separated from any source of mercury vapor by a trap immersed in dry ice. Otherwise, mercurous bromide will gradually be deposited on the windows and change their transmission. The hydrogen bromide may be frozen with liquid air and the pressure of hydrogen formed due to illumination may be ascertained. The same type of calculation as that given for the uranyl sulfate – oxalic acid actinometer should be used. One molecule of hydrogen is formed per quantum absorbed ($\Phi = 1$ in equations (19) and (20) above), but correction is usually necessary for a small thermal reaction with the mercury. The amount of hydrogen bromide decomposed should remain below 1%.

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[31] Hunt and Hill, *J. Chem. Phys.*, **15**, 111 (1947).

[32] Noyes, *J. Chem. Phys.*, **5**, 809 (1937).

The *hydrogen iodide actinometer*[33] can be used to longer wave lengths (about 3000 Å.) than the hydrogen bromide actinometer, but it is generally less useful because of the greater thermal instability of the hydrogen iodide and its greater tendency to react with mercury. Again one molecule of hydrogen is formed per quantum absorbed.

Ozone synthesis is useful only at short wave lengths, below the limit of transmission of quartz. In this case two molecules of ozone are formed per quantum absorbed of oxygen, but a flow system must be used since light also causes the decomposition of ozone. Hence this actinometer is not to be recommended except in cases where no other method of measurement is available.

At short wave lengths, particularly with the two xenon lines at 1295 and 1470, the *decomposition of carbon dioxide* has been used as an actinometer.

V. FACTORS INFLUENCING DESIGN OF PHOTOCHEMICAL APPARATUS

1. Effect of Absorption Coefficient and of Type of Absorption

It must always be remembered in dealing with photochemical systems that there is no advantage and indeed there may be serious disadvantages to having a reaction vessel thicker than that necessary to give about 75% absorption. The light is absorbed to the greatest extent near the window of incidence, and the layers on the opposite side of the vessel may receive inadequate exposure for complete reaction. It is obvious that the greatest percentage conversion in a static system will be produced in a thin vessel in which all parts receive essentially the same radiation. The alternative is to use a thicker vessel giving a higher percentage of absorption and consequently a more efficient use of the light source but with sufficient stirring so that all parts of the reaction system receive roughly equivalent exposures to the light.

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[33] Warburg, *Sitzber. preuss. Akad. Wiss.*, **1916**, 314. Lewis, *Proc. Natl. Acad. Sci. U. S.*, **13**, 720 (1927).

If the light is polychromatic, usually a wide range of absorption coefficients will be found. The absorption coefficient is defined by the equation:

$$kcd = \ln (I_0/I) \tag{21}$$

where k is the absorption coefficient, c is the concentration in suitable units, d is the thickness of the cell, I_0 is the incident intensity of the radiation, and I is the intensity of the transmitted radiation; k is constant only at a given temperature for strictly monochromatic light and then only if the molecular species are independent of concentration. Thus NO_2 is colored whereas N_2O_4 is transparent to visible light. At high pressures the system $2\ NO_2 \rightleftharpoons N_2O_4$ is more transparent than at low pressures. Similar but less definite changes in molecular species occur in other systems, thus invalidating the simple absorption equation given above (see West in Part II, 2nd edition, *Physical Methods of Organic Chemistry*[33a]).

For most synthetic organic work monochromatic light will not be used, and hence a small amount of experimentation will be necessary to determine optimum conditions. If it is not convenient to use cells of more than one thickness to determine whether the yield is greater for thicker cells, the concentration may be varied. The highest percentage conversion in unit time is to be desired.

Let us consider a specific case in which a reaction between some organic molecule and chlorine is taking place in a solvent, such as carbon tetrachloride. The absorption coefficient of chlorine in such a solution is low in the red and rises until it reaches a maximum in the neighborhood of 4000 Å. after which it gradually decreases.[34] If the concentration of the chlorine is about 1 mole per liter, it can be shown that at 4358 Å. well over 99% of the radiation is absorbed in a thickness of 1 centimeter. At 3500 and 4500 Å. the percentage is less, and at 3000 and at 5500 Å. there is little or no absorption. There will be some gain in the total amount of radiation absorbed from sunlight if the cell is over about 2 cm. thick, but by increasing the thickness either the amount of unreacted material will increase, or the exposure time for complete reaction will be increased even if the system is thoroughly stirred.

[33a] Interscience, New York.

[34] Leermakers and Dickinson, *J. Am. Chem. Soc.*, **54**, 4648 (1932). Dickinson and Carrico, *ibid.*, **56**, 1473 (1934).

2. Flow and Static Systems

If the chemical system under investigation undergoes only a single reaction under the influence of light, a static system may be used. An investigation with careful analytical determinations of all products, using varying times of exposure, will be necessary to prove this to be the case. With complex organic molecules the products of the reaction may absorb in the same region of the spectrum as the parent substance, and consequently there may either be secondary or reverse reactions. To cite a simple example, maleic acid may be converted into fumaric acid and fumaric acid may be converted into maleic acid by the same wave length.[35] Consequently the reaction will never go to completion, and the ratio of maleic to fumaric acid will depend upon the time of exposure, approaching a constant value which depends somewhat on the wave length.

Reactions involving the addition of chlorine to double bonds will invariably be accompanied by some substitution if the molecules also have carbon-hydrogen bonds. Usually the addition reaction is the more rapid of the two, but if one wishes to minimize substitution, either the exposure must be short, or the system must be circulated in front of the light source so that the addition compound is removed rapidly from the illuminated zone. Obviously it is necessary to compromise between completeness of reaction and initiation of undesired reactions. A certain amount of experimentation with the system is necessary for the determination of optimum conditions.

A flow system which merely provides recirculation of the same material over and over again through the illuminated zone will not usually serve to eliminate undesirable reactions. However, the

[35] Warburg, *Sitzber. preuss. Akad. Wiss.*, **1919**, 360.

effects of concentration of intermediate free radicals and atoms may not be the same for all reactions occurring in the system. For example, if the desired product is formed by reaction between two free radicals, each one of which has a concentration proportional to the intensity, the over-all rate will be proportional to the square of the intensity in a static system. If some undesired reaction has a rate dependent upon the first power of the intensity in a static system, its rate would be the same whether the system were flowing or not. Since free radicals would be swept along in a flow system, their concentrations fall off in the nonilluminated zone. Thus, a flow system would tend to give a lower relative yield of the desired product than a static system.

All variations of these effects may be found in practice, and it will be necessary for the experimenter to study all factors if he desires to ascertain conditions for obtaining optimum yields.

3. Temperature Regulation

Change of temperature may affect the rate of photochemical reactions for one or more of the following reasons: (*a*) the absorption coefficient may change with temperature; (*b*) the rates of secondary reactions may depend markedly on temperature in much the same way as the rates of ordinary thermal reactions; and (*c*) the yield of the primary process may also depend on temperature, although this effect is usually less important than the other two.

If the light beam covers a broader band of wave lengths than is absorbed by the reacting molecules, the amount of light absorbed may vary little with temperature. Thus the total absorption of sunlight by gaseous chlorine at a given concentration will change little with temperature provided that the absorption is only a few per cent at the wave length of maximum absorption. The effect of increasing the temperature is to broaden the absorption band and to decrease the absorption at the maximum. The value of $\int E_\lambda \, d\lambda$ will be almost independent of temperature, where E_λ is the energy absorbed at wave length λ per second per cubic centimeter (see Fig. 3). If, on the other hand, the pressure of the chlorine or the thickness of the layer is such that complete absorption is observed at 4000 Å., increase of temperature will increase the total absorption because the absorption will remain complete at 4000 Å. and also become increasingly important at other wave lengths. This is shown schematically in Figure 3.

If the light source is monochromatic, the percentage absorption will increase or decrease with increase in temperature depending on where the wave length falls in the absorption band. If the line of the light source falls right at the peak, increase in temperature will cause a decrease in light absorption unless the latter is so high that it always approximates 100%. At wave lengths sufficiently removed from the peak, and more particularly at longer wave lengths than that of the peak, increase in temperature will cause an increase in absorption. This effect can be seen qualitatively by a study of Figure 3.

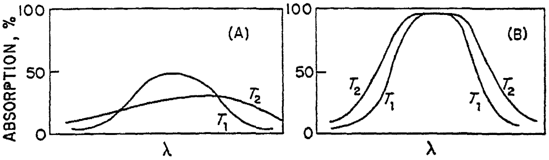

Fig. 3. Schematic representation of temperature effect on light absorption with polychromatic light. $T_2 > T_1$. (A) Absorption is incomplete at all wave lengths; the areas under the two curves are approximately the same. (B) Absorption is complete over part of the region; in this case increase in temperature increases the area under the curve.

A little experimentation is necessary before one can decide whether any real benefits can be derived by change in temperature.

The temperature coefficients of secondary reactions may sometimes be estimated by analogy. For example, if methyl radicals are produced during the absorption of light by the parent molecule, they will have little tendency to form methane by removing hydrogen from aliphatic compounds containing hydrogen at room temperature. As the temperature is raised, the amount of methane increases quite rapidly indicating that the heat of activation for reactions of the type:

$$CH_3 + RH \rightarrow CH_4 + R \qquad (22)$$

is fairly high. In a complex organic system in which free radicals may undergo a variety of reactions for which the temperature coefficients differ, it is evident that the composition of the products may vary markedly with the temperature. To cite a simple example;

Exposure of acetone to radiation of about 3000 Å. leads to appreciable quantities of biacetyl and ethane at room temperature.[36] At temperatures of 100°C. and above the amount of biacetyl formed is negligible and the main products are ethane and carbon monoxide. At still higher temperatures the amount of methane increases markedly and other products must be formed. The acetyl radical becomes quite unstable at high temperatures and cannot last long enough to form biacetyl.

The effect of temperature on the primary process is more difficult to predict and to describe. If the light energy absorbed by a molecule is insufficient to produce dissociation, increase in temperature may permit a certain fraction of the molecules to make up the deficiency from thermal energy. In other cases molecules already possessing thermal energy may dissociate following absorption of light which could not dissociate "cold" molecules. Thus 5000 Å. will not dissociate chlorine at low temperatures, but at higher temperatures, even at 100°C., enough chlorine molecules possess vibration energy due to thermal motion to permit considerable dissociation at that wave length.

The main conclusion one can draw from this brief discussion is that in complex organic reactions the temperature may have a very large effect both on the nature of the products and on their rates of formation. Data on these matters for reactions involving complex molecules are very meager, but before embarking on an extensive synthetic program a systematic study of the reaction should be made.

4. Effect of Intensity

There are other factors than temperature that affect both the rate of the reaction and the purity of the product. For example, in a chlorination reaction the primary process is the dissociation of chlorine into atoms. The rate of the desired reaction may be dependent on the concentration of atoms. The following processes cause formation and removal of chlorine atoms:

$$Cl_2 + \text{light} \rightarrow 2\,Cl \qquad +d(Cl)/dt = k_1 I \tag{23}$$

$$Cl + Cl \rightarrow Cl_2 \qquad -d(Cl)/dt = k_2(Cl)^2 \tag{24}$$

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[36] Barak and Style, *Nature*, **135**, 307 (1935). Spence and Wild, *J. Chem. Soc.*, **1937**, 352.

When the rate of formation of atoms becomes equal to their rate of recombination:

$$k_1 I = k_2(\mathrm{Cl})^2 \tag{25}$$

$$(\mathrm{Cl}) = (k_1 I/k_2)^{1/2} \tag{26}$$

Parentheses indicate concentrations.

If the rate of formation of products is proportional to the concentration of chlorine atoms, the rate will evidently vary with the square root of the intensity. Since for a given incident light intensity the amount of light absorbed per unit volume increases with the concentration, the rate will also vary with the square root of the chlorine concentration until the latter is so high that absorption is quite high.

In a system where the absorption is high, many atoms will be formed near the window where the light enters the cell, and the number will fall off as the distance from the window increases, becoming zero at sufficient distance. Consequently the rate of any chlorination reaction will not be uniform throughout the reaction vessel unless the atoms last a long time before they disappear.

If two reactions can occur simultaneously, one of which depends on the square root of the intensity, and the other on some other power, the nature of the product may also be determined by the light intensity. A hypothetical example of the effect of intensity when two reactions occur simultaneously may be given. Suppose there are two ways of using chlorine atoms, one by equation (24) above and the other a removal by some molecule X in the system which leads to an undesired product. The desired product is formed by a chain reaction whose rate is proportional to the chlorine atom concentration but which regenerates chlorine atoms. The series of events is:

$$\mathrm{Cl_2} + \text{light} \rightarrow 2\,\mathrm{Cl} \qquad \text{Rate} = k_1 I \tag{23}$$

$$\mathrm{Cl} + \mathrm{M} \rightarrow \mathrm{MCl} \qquad = k_3(\mathrm{Cl})(\mathrm{M}) \tag{27}$$

$$\mathrm{MCl} + \mathrm{Cl_2} \rightarrow \mathrm{MCl_2} + \mathrm{Cl} \qquad = k_4(\mathrm{MCl})(\mathrm{Cl_2}) \tag{28}$$

$$\mathrm{Cl} + \mathrm{X} \rightarrow \mathrm{ClX} \qquad = k_5(\mathrm{Cl})(\mathrm{X}) \tag{29}$$

$$\mathrm{Cl} + \mathrm{Cl} \rightarrow \mathrm{Cl_2} \qquad = k_2(\mathrm{Cl})^2 \tag{24}$$

MCl_2 is the desired product and ClX is the by-product not desired. By placing rate of formation of Cl atoms equal to rate of disappearance, and rate of formation of MCl equal to rate of disappearance, one finds the ratio of MCl_2 formed to ClX formed to be independent of intensity and dependent only on the ratio (M)/(X). If, however, the desired product were formed by the reaction:

$$Cl + Cl + M \rightarrow MCl_2 \qquad k_6(M)(Cl)^2 \qquad (30)$$

the rate of formation of MCl_2 would depend on $(Cl)^2$ and that of ClX on (Cl). Hence a high intensity would give proportionately more MCl_2 than a low intensity.

5. Effect of Vessel Dimensions

For reasons which are obvious from the preceding discussion concentration may markedly affect the nature of the products. For example, if acetone dissociates into methyl and acetyl radicals under the influence of light, and acetyl radicals form biacetyl on the walls, then a decrease in pressure—meaning an increase in the rate of diffusion to the walls—will mean an increase in biacetyl formation. If on the other hand, two acetyls must collide in the gas phase to form biacetyl, the rate will be dependent on the square of the light intensity and anything which prevents diffusion to the walls, such as a high pressure, would tend to increase the rate of formation of biacetyl. Actually both of these processes must be taken into account in the complete description of the behavior of acetone photochemically.

Many atoms and radicals are removed when they collide with the walls. A chain reaction will usually go more rapidly in a vessel with a large ratio of volume to surface provided that the light is absorbed uniformly throughout the vessel and not mostly near one window. Sometimes a high pressure which confines the absorption to a region near the window will have the same effect as decreasing vessel dimensions. Each reaction must be studied with the possible retarding effect of the walls in mind. In few instances do the walls accelerate a photochemical reaction.

6. Effect of Impurities

Impurities often play a decided part both in the yield of a photochemical reaction and in the nature of the product. These effects may be due to: (*a*) a light filter action in which the impurities absorb light in preference to the molecule the reactions of which are desired; (*b*) impurities may react with some of the atoms and free radicals and hence change the character of the secondary reaction. This phenomenon is particularly troublesome in dealing with the halogens, but it is undoubtedly important in many other cases; and (*c*) impurities by reacting with some of the intermediates may effectively change their concentrations thus producing effects analogous to changes in intensity. Hence, the relative amounts of products might be affected considerably by small amounts of impurities.

Oxygen is a strong inhibitor for many chlorinations, presumably because it reacts with chlorine atoms. The concentration of chlorine atoms in such a case might be proportional to intensity (not the square root) and inversely proportional to the oxygen pressure.

It can be seen from the foregoing that control of *temperature*, of *concentration or pressure*, of *intensity*, and of *vessel size* may be important in obtaining reproducible photochemical results. However, it should be mentioned that, there are many reactions, the courses of which are not too sensitive to these variables.

VI. TYPES OF PHOTOCHEMICAL REACTIONS

1. Behavior of Organic Compounds on Irradiation

A. WAVE LENGTH NECESSARY FOR ABSORPTION

Pure saturated hydrocarbons are quite transparent until one reaches short wave lengths. Simple unsaturated hydrocarbons with one double bond (*e.g.*, ethylene, propylene, etc.) absorb at wave lengths below about 2200 Å., but appreciably only beyond the limits of quartz.[37] Compounds containing two double bonds not conjugated absorb at about the same wave length, but conjugated systems have absorptions at longer wave lengths. Acetylene absorbs also up to wave lengths slightly longer than 2000. It may be that simple hydrocarbons not containing aromatic groups react photochemically only toward the limit of transmission of quartz or beyond unless excited mercury atoms are present.

The absorptions of other molecules depend both on the polar groups which are present and on the structure of the molecule. Thus if one examines the simple aliphatic acids, formic, acetic, propionic, butyric, etc., in aqueous solution, one finds that, whereas formic acid absorbs[38] up to wave lengths of 3000 Å., the others absorb[39] mainly below 2500 Å. From acetic on to higher members, the wave length at which optical absorption becomes noticeable is not very dependent on the number of CH_2 groups in the molecule and, indeed, at a given concentration in moles per liter the light absorptions are of the same order of magnitude.

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[37] Price, *Phys. Rev.*, **47**, 444 (1935).

[38] Gorin and Taylor, *J. Am. Chem. Soc.*, **56**, 2042 (1934).

Statements analogous to those for the acids can be made for other homologous series, such as methylamine, ethylamine, etc.[40] Usually the first member of each series is somewhat anomalous in its absorption spectrum just as it is apt to be in its chemical properties. Thus each group, such as CH_2NH_2, CH_2OH, CO_2H, CH_2SH, has a characteristic absorption region relatively independent of the size of the alkyl radical to which it is attached.

Aromatic compounds, if they are simple, such as benzene, toluene, xylene, etc., also show absorption in quite similar regions of the spectrum.[40] If, however, we deal with a complex molecule which contains more than one polar group or more than one aromatic nucleus, the spectrum may become quite difficult to interpret.

As a general rule two polar groups in the same molecule act quite independently if they are separated by some distance.[40] Thus glutaric acid will show just about twice the absorption at a given molar concentration as will propionic acid. In this case each carboxyl absorbs in its own right and is not affected greatly by the presence of another one in the same molecule. Oxalic acid, however, in which the two carboxyl groups are adjacent to each other, absorbs at much longer wave lengths, indeed, as high as 3500 Å. As a general rule the two polar groups show characteristic absorptions which are displaced toward longer wave lengths the closer they are together in the molecule.

B. REACTIONS OF KETONES

The simple aliphatic ketones[41] absorb in the general region from 2300 to 3200 Å. The general forms of the absorption curves are about the same for all, both in solution and in the gas phase, and the amount of light absorbed for a given molar concentration is also nearly but not quite independent of the size of the alkyl groups. However, the reactions these ketones undergo do vary markedly from one to another.

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[39] *Cf.* Pierce and Morey, *J. Am. Chem. Soc.*, **54**, 467 (1932). *Cf.* Rollefson and Burton, *Photochemistry*, Prentice-Hall, New York, 1939, p. 363.

[40] Tables of spectra of organic compounds may be found in the various volumes of *Tables Annuelles de Constantes et Donnêes Numeriques* and in the *International Critical Tables*, McGraw-Hill, New York, 1925. Other summaries have been published from time to time in *Chemical Reviews* and by Victor Henri.

[41] *Cf.* Davis, Jr., *Chem. Revs.*, **40**, 201 (1947) for a review.

As pointed out previously (pp. 91, 101), acetone gives ethane, carbon monoxide, and biacetyl, the amount of biacetyl being quite dependent on experimental conditions. Diethyl ketone gives carbon monoxide, some butane, some ethane, and perhaps, under certain conditions, some ethylene.[42] If the temperature is raised above 100°C., however, the amount of ethylene seems to be very small, and the amount of ethane unduly large. This must mean that ethyl radicals react with diethyl ketone molecules to form ethane. There would be simultaneous production of other molecules not yet analyzed for. Ketones with aliphatic groups larger than propyl seem to undergo relatively little of the customary reactions in which carbon monoxide is produced, but instead undergo cleavage at the carbon-carbon bond once removed from the carbonyl group. Thus methyl *n*-butyl ketone, when exposed to radiation near 3000 Å., gives appreciable amounts of acetone and propylene.[43] This behavior illustrates that in photochemical reactions reasoning by analogy from one member of a homologous series to another is not always safe. In general the multiplicity of products obtained in the photochemical decomposition of the simple aliphatic ketones greatly limits the usefulness of the reaction for synthetic purposes.

Cyclic ketones on irradiation with ultraviolet light give carbon monoxide and several hydrocarbons.[44,45] Thus cyclohexanone gives carbon monoxide and the pentamethylene diradical, which mainly isomerizes to cyclopentane and pentene-1 but also cleaves to give small amounts of ethylene and propylene.[45] Cyclopentanone yields carbon monoxide, ethylene, and cyclobutane. The yield of cyclobutane is 38% and, in view of the difficulties of preparing cyclobutane by other methods, the reaction has some promise as a method of synthesis of cyclobutane.[45]

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[42] Ells and Noyes, *J. Am. Chem. Soc.*, **61,** 2492 (1939).

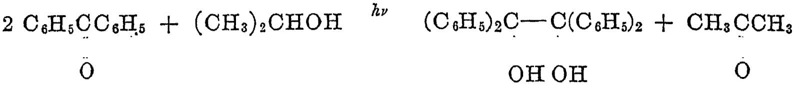
[43] Norrish, *Trans. Faraday Soc.*, **33,** 1521 (1937). Bamford and Norrish, *J. Chem. Soc.*, **1938,** 1531. Davis and Noyes, *J. Am. Chem. Soc.*, **69,** 2153 (1947).

[44] Saltmarsh and Norrish, *J. Chem. Soc.*, **1935,** 455. Bamford and Norrish, *ibid.*, **1938,** 1521.

[45] Benson and Kistiakowsky, *J. Am. Chem. Soc.*, **64,** 80 (1942).

In aqueous solution in sunlight cyclohexanone has the ring broken and the elements of water added, giving caproic acid in small yield.[46] This type of reaction of cyclic ketones seems to be quite general.[47]

Aryl ketones are reduced by alcohols in the presence of sunlight or ultraviolet light to give benzpinacols and the aldehyde or ketone corresponding to the alcohol employed.[48] Thus the reduction of benzophenone by isopropyl alcohol[49] is illustrated by the equation:



$$2\ C_6H_5\underset{\overset{\|}{O}}{C}C_6H_5 + (CH_3)_2CHOH \xrightarrow{h\nu} (C_6H_5)_2\underset{OH}{C}\text{—}\underset{OH}{C}(C_6H_5)_2 + CH_3\underset{\overset{\|}{O}}{C}CH_3$$

Many differently substituted benzophenones have been employed in this reaction and the yields are almost uniformly good.[49,50] Various alcohols may be used for the reduction; however, isopropyl alcohol because of its availability and the fact that it yields a stable ketone is the most frequent choice. Although sunlight is the usual radiation employed, the reaction proceeds more rapidly with radiation from a mercury arc, the rate being dependent on the intensity. Recently it has been shown that ketones other than strictly aromatic ones, including acetone, acetophenone, indanone, phenyl benzyl ketone and 1,4-diphenylbutanone can be converted to the corresponding pinacols in good yield.[50]

Procedure for Benzopinacol.[51] A mixture of benzophenone (150 g., 0.82 mole), 1 drop of glacial acetic acid, and isopropyl alcohol (850 cc., 11 moles) is warmed to 45° in a 1-liter round-bottom flask. The flask is closed with a tight cork firmly wired or tied in place, and is inverted and exposed to direct sunlight. Crystals of benzopinacol begin to appear after three to five hours; and after eight to ten days of exposure the flask is filled with crystals of benzopinacol. The yield of practically pure benzopinacol, m.p. 188–190°, obtained by filtration is 141–142 g. (93–94% of the theoretical amount).

Certain of the aromatic ketones, such as fluorenone,[49] xanthone,[50] α-naphthyl phenyl ketone,[50] and di-α-naphthyl ketone,[50] undergo no

[46] Ciamician and Silber, *Ber.*, **41**, 1071 (1908).

[47] *Cf.* Noyes and Leighton, *The Photochemistry of Gases.* Reinhold, New York, 1941, p. 429.

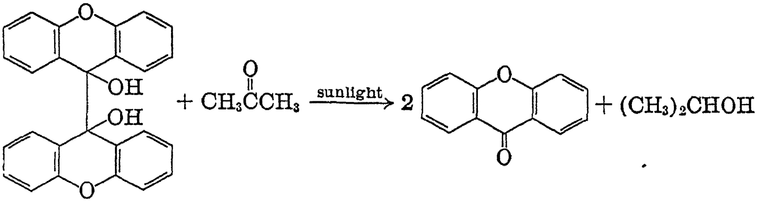
[48] For a summary see Schönberg and Mustafa, *Chem. Revs.*, **40**, 181 (1947).

[49] Bachmann, *J. Am. Chem. Soc.*, **55**, 391 (1933).

[50] Weizmann, Bergmann, and Hirshberg, *J. Am. Chem. Soc.*, **60**, 1530 (1938). Bergmann and Hirshberg, *ibid.*, **65**, 1429 (1943).

[51] Blatt, *Organic Syntheses.* Coll. Vol. II, Wiley, New York, 1943.

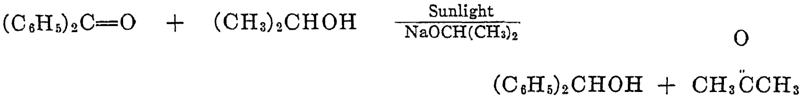
reaction with alcohols on irradiation. In contrast it has been found that fluorenopinacol and xanthopinacol on exposure to light in the presence of acetone give fluorenone and xanthone, respectively, the acetone being reduced to isopropyl alcohol.[52] This is illustrated for



Xanthopinacol

xanthopinacol. It is quite possible that the reaction of aromatic ketones with alcohols in the presence of light leads to an equilibrium which may in one case favor the formation of the pinacol and in another case may favor the formation of the aromatic ketone.

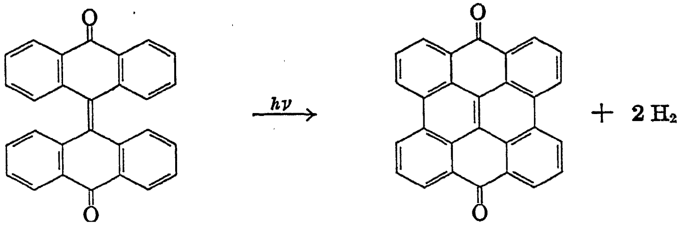
Bachmann[49] has shown that in the presence of sodium alkoxides the reaction of aromatic ketones with alcohols yields not the corresponding pinacols but rather the benzhydrols:



$$(C_6H_5)_2C{=}O \quad + \quad (CH_3)_2CHOH \quad \xrightarrow[\text{NaOCH(CH}_3)_2]{\text{Sunlight}} \quad (C_6H_5)_2CHOH \; + \; CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3$$

The yields are practically quantitative and the reaction has preparative value.

Certain aromatic ketones undergo unusual dehydrogenation in the presence of sunlight to form compounds with a highly condensed aromatic ring system.[48] An example of this type of photodehydrogenation is the formation of naphthadianthrone[53] as given in the following equation:



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[52] Schönberg and Mustafa, *J. Chem. Soc.*, **1944**, 67.
[53] Meyers, Bondy, and Eckert, *Monatsh.*, **33**, 1447 (1912).

C. REACTIONS OF ALDEHYDES

All aldehydes absorb in the relatively near ultraviolet, *i.e.*, from 3300 or 3400 Å. to below 2500 Å. Saturated aldehydes invariably give carbon monoxide, but other compounds are synthesized simultaneously in rather low yields. Thus acetaldehyde, in addition to carbon monoxide and methane, gives some biacetyl, glyoxal, and perhaps methylglyoxal.[54] The yields of these latter compounds decrease as the temperature is raised. Unsaturated aldehydes, such as acrolein and crotonaldehyde, undergo polymerization and do not give the reactions common to the saturated aldehydes. From the synthetic standpoint these reactions present little of interest.

The aromatic aldehydes undergo many of the same reactions discussed previously for aromatic ketones. Thus, benzaldehyde and anisaldehyde on irradiation in alcohol give the corresponding pinacols.[55]

D. REACTIONS OF ESTERS

Simple esters, such as methyl formate,[56] methyl acetate,[57] etc., split out carbon dioxide, but the reaction is not simple, and a wide variety of products is formed. A mercury arc lamp must be used together with quartz apparatus, as such esters absorb only quite far in the ultraviolet. More complex esters undergo reactions of some interest, but the data are qualitative and probably not very reliable.

E. REACTIONS OF AMINES AND NITROGEN COMPOUNDS

The simple amines, such as methylamine, give ammonia, hydrogen, nitrogen, and a series of hydrocarbons.[58–60] With oxygen present methylamine gives some carbon monoxide and formaldehyde.[60] The simple amino acids seem to decompose quite completely in the presence of sunlight, but little information is available concerning the complex ones.

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[54] Blacet and Moulton, *J. Am. Chem. Soc.*, **63,** 868 (1941), and a series of other references in the same journal.

[55] Ciamician and Silber, *Ber.*, **34,** 1530 (1901).

[56] Volman, *J. Am. Chem. Soc.*, **64,** 1820 (1942).

[57] Royal and Rollefson, *J. Am. Chem. Soc.*, **63,** 1521 (1941).

[58] Emeleus and Taylor, *J. Am. Chem. Soc.*, **53,** 3370 (1931).

[59] Wetmore and Taylor, *J. Chem. Phys.*, **12,** 61 (1944).

[60] Emeleus and Jolley, *J. Chem. Soc.*, **1935,** 1612.

The cyanides and nitriles are light sensitive, although usually only in the ultraviolet. Triphenylmethyl cyanide in solution is apparently converted by irradiation to the carbonium salt.[61] Most of these reactions are complex, and since they have not been studied with monochromatic light, it is not known whether they could be made useful or not.

F. REACTIONS OF PEROXIDES

Peroxides, if present, often alter the course of reactions. They mostly decompose to give free radicals and oxygen, the free radicals being capable of initiating other reactions. In some cases the peroxides undergo a more or less complete disintegration with the formation of appreciable quantities of carbon dioxide.

Only one or two simple examples need be cited. Diethyl peroxide when exposed to radiation from a mercury arc gives ethyl alcohol and biacetyl.[62] Biacetyl peroxide reacts rapidly under the same conditions, but the nature of the products depends on the solvent used.[63] In cyclohexane solution carbon monoxide, carbon dioxide, oxygen, methane, ethane, and various unsaturated compounds have been found. Dibenzoyl peroxide gives carbon dioxide, biphenyl, and a resin.[64]

G. REACTIONS OF CARBON MONOXIDE[65]

Carbon monoxide itself is transparent to the quite far ultraviolet' and hence reactions involving its absorption can only be carried out with fluorite or with lithium fluoride windows, and special light sources, such as the xenon arc. However, there are instances when free radicals seem to react with the carbon monoxide. Thus in the far ultraviolet the synthesis of acetone has been reported from mixtures of ethane and carbon monoxide.[66] This type of reaction has not been studied extensively, but it is possible that further investigations of such systems would be of interest.

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[61] Lifschitz, *Ber.*, **58**, 2434 (1925).

[62] Barak and Style, *Nature*, **135**, 307 (1935).

[63] See Noyes and Leighton, *The Photochemistry of Gases*. Reinhold, New York, 1941, p. 436.

[64] Fichter and Schnider, *Helv. Chim. Acta.*, **13**, 1428 (1930).

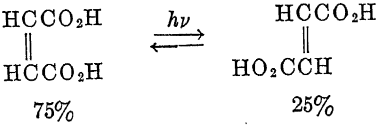
[65] Groth, *Z. physik. Chem.*, **B37**, 315 (1937).

[66] Faltings, *Ber.*, **72**, 1207 (1939).

H. REACTIONS OF UNSATURATED COMPOUNDS

Isomerization. Geometrical isomers of the *cis-trans* type can be interconverted when their solutions are irradiated with ultraviolet light. The explanation for this is not clearly established. The absorption of light by the ethylenic bond may lead to an excited state in which rotation is no longer restricted,[67] or some photodecomposition may occur giving free readicals or atoms, which in turn effect the isomerization.[68] Actually isomerization can probably occur by either of these ways depending on the wave length used.

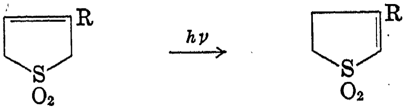
Isomerization usually favors formation of the less stable isomer, but after sufficient exposure an apparent photoequilibrium is attained. Thus irradiation of either fumaric or maleic acid yields the same mixture of about 75% maleic acid (the *cis* form) and 25% fumaric acid (the *trans* form):[67, 69]



$$\begin{array}{c}\mathrm{HCCO_2H}\\ \| \\ \mathrm{HCCO_2H}\\ 75\%\end{array} \;\underset{\longleftarrow}{\xrightarrow{h\nu}}\; \begin{array}{c}\mathrm{HCCO_2H}\\ \| \\ \mathrm{HO_2CCH}\\ 25\%\end{array}$$

Similarly many other ethylenic compounds, such as cinnamic acid,[70] substituted cinnamic acids,[70] stilbene,[71] and dichloroethylene,[72] have been isomerized to equilibrium mixtures by irradiation. Oximes and azo compounds behave analogously.[73]

Irradiation of certain ethylenic compounds may cause isomerization by a shifting of the double bond. This behavior is typical of unsaturated cyclic sulfones:[74]



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[67] See Rollefson and Burton, *Photochemistry and the Mechanism of Chemical Reactions*. Prentice-Hall, New York, 1939, p. 248.

[68] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[69] Olson and Hudson, *J. Am. Chem. Soc.*, **55**, 1410 (1933).

[70] Stoermer, *Ber.*, **44**, 637 (1911); **42**, 4865 (1909).

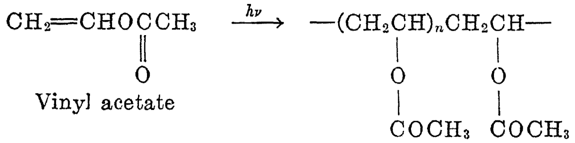
[71] Lewis, Mayel, and Lipkin, *J. Am. Chem. Soc.*, **62**, 2973 (1940).

[72] Mahncke and Noyes, *J. Am. Chem. Soc.*, **58**, 932 (1936). Olson and Maroney, *ibid.*, **56**, 1320 (1934).

[73] Winkel and Siebert, *Ber.*, **74**, 670 (1941).

[74] Backer and Strating, *Rec. trav. chim.*, **54**, 618 (1935).

Polymerization. Most dienes and ethylenic compounds can be polymerized if irradiated by light of suitable wave length. There are two obvious ways in which polymerization can occur. The absorption of light may result in rupture of the ethylenic linkage to yield a diradical which initiates polymerization, *or* the absorption of light may cause some photodecomposition giving free radicals or atoms which initiate polymerization. In any case experimental evidence indicates a close relationship between photochemical polymerization and free radical polymerization. For instance in the photopolymerization of vinyl acetate the head-to-tail type polymer obtained is the same as that from peroxide-induced polymerization.[75]



$$CH_2{=}CHO\underset{\substack{\| \\ O}}{C}CH_3 \xrightarrow{h\nu} -(CH_2\underset{\substack{| \\ O \\ | \\ COCH_3}}{CH})_nCH_2\underset{\substack{| \\ O \\ | \\ COCH_3}}{CH}-$$

Vinyl acetate

The rate of polymerization and also the length of the polymer chain produced are dependent on the nature and concentration of the monomer, light intensity, and wave length. High concentrations favor faster rate of chain growth and longer chain length whereas at low concentrations the slower rate gives greater opportunity for chain-terminating reactions to occur. Ordinarily a very high light intensity is not desirable since the simultaneous initiation of many chains tends to result in shorter chain length. In the photopolymerization of vinyl acetate it was found that for each quantum of light absorbed approximately one polymer molecule was formed.[76]

The wave length of light necessary for polymerization varies considerably from one monomer to another. The simple vinyl halides require radiation[75,77] of 2100 to 2800 Å., whereas vinyl acetate,[75,76] acrylic acid derivatives,[78] and dienes[79] can be polymerized by radiation of 3000 to 6000 Å. In order to effect polymerization with light of long enough wave length to permit the use of pyrex apparatus, materials such as acetone[80] and hexachloroethane[79] are often added. Such materials decompose photochemically to give free radicals which then initiate polymerization.

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[75] Marvel and Riddle, *J. Am. Chem. Soc.*, **62**, 2666 (1940). Marvel and Levesque, *ibid.*, **61**, 3244 (1939).

[76] Melville and Burnett, *Nature*, **156**, 661 (1945).

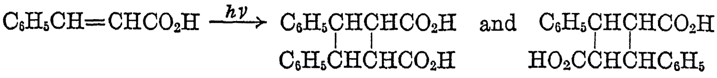
[77] Newkirk, *J. Am. Chem. Soc.*, **68**, 2467 (1946). Jones and Melville, *Proc. Roy. Soc. London*, **A187**, 39 (1946).

[78] Agre, U. S. Pat. 2,367,660 (Jan. 23, 1945); *Chem. Abstracts*, **39**, 3703 (1945).

[79] Dreisback, U. S. Pats., 2,386,447 and 2,386,448 (Oct. 9, 1945); *Chem. Abstracts*, **40**, 761, 762 (1946).

Polymerization may be done in either the gas[76] or the liquid phase,[75] although preparative work is almost always done in the liquid phase. In the laboratory the usual procedure is merely to place a solution of the material in a sealed quartz or Pyrex tube in a beam of ultraviolet light. Industrially, large constant-temperature reactors having a source of internal radiation are usually employed.[81]

Dimerization. Certain ethylenic compounds when irradiated in the solid state undergo dimerization to form cyclobutane derivatives.



$$C_6H_5CH{=}CHCO_2H \xrightarrow{h\nu} \begin{array}{l} C_6H_5\underset{|}{C}H\underset{|}{C}HCO_2H \\ C_6H_5CHCHCO_2H \end{array} \quad \text{and} \quad \begin{array}{l} C_6H_5\underset{|}{C}H\underset{|}{C}HCO_2H \\ HO_2CCHCHC_6H_5 \end{array}$$

Cinnamic acid **Truxinic acid** **Truxillic acid**

For example, cinnamic acid in sunlight yields the isomeric truxinic and truxillic acids. Either of the geometric isomers of cinnamic acid can be converted to either truxinic or truxillic acid depending on how the cinnamic acids were handled prior to irradiation.[82] Substituted cinnamic acids[83] give analogous reactions as do also the similarly constituted ketones, benzalacetophenone,[84] and benzalpyruvic ester.[85]

I. MOLECULAR REARRANGEMENTS

The absorption of light by certain molecules results in highly unusual rearrangements. A few examples of such rearrangements are given below. For the most part the mechanisms of these rearrangements are not at all clearly understood.

The irradiation of *o*-nitrobenzaldehyde in the solid state or in solution by light of 3130 to 4360 Å. gives *o*-nitrosobenzoic acid in good yield and with few side products.[86] Substituted *o*-nitrobenzaldehydes show analogous reactions, but *m*- and *p*-nitrobenzaldehydes give no reaction at all.[86]

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[80] Jones and Melville, *Proc. Roy. Soc. London*, **A187**, 19 (1946).

[81] Ellis and Wells, *Chemical Action of Ultraviolet Rays*. Reinhold, New York, 1941, p. 409.

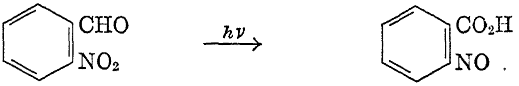
[82] Bernstein and Quimby, *J. Am. Chem. Soc.*, **65**, 1845 (1943).

[83] Stobbe, *Ber.*, **58**, 2859 (1925).

[84] Stobbe and Hensel, *Ber.*, **59**, 2254 (1926).

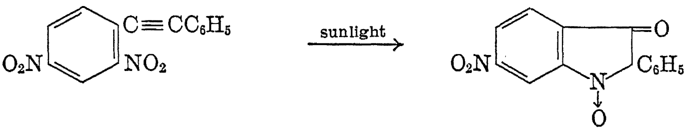
[85] Reimer, *J. Am. Chem. Soc.*, **46**, 783 (1924).

[86] Leighton and Lucy, *J. Chem. Phys.*, **2**, 756, 760 (1934).



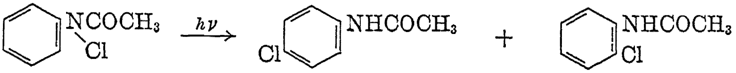
o–Nitrobenzaldehyde *o*-Nitrosobenzoic acid

A somewhat similar reaction is the rearrangement of 2,4-dinitrotolan to 2-phenylisatogen.[87]



2,4-Dinitrotolan 2-Phenylisatogen

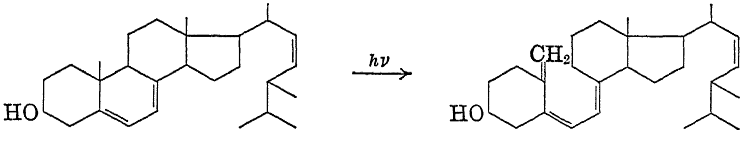
Rearrangement of *N*-chloroacetanilide to a mixture of *o*- and *p*-chloroacetanilides occurs readily in sunlight or ultraviolet light.[88]



N-Chloroacetanilide

The rate of reaction is markedly dependent on the nature of the solvent and on the acidity. A similar rearrangement occurs with *N*-chlorobenzanilide.[89]

Undoubtedly the most important photochemical rearrangement is that of ergosterol to vitamin D_2. This reaction is best accomplished



Ergosterol Vitamin D_2 (calciferol)

with light of 2810 Å. and involves several intermediate steps. Detailed discussions of the irradiation of ergosterol and other related sterols are available elsewhere.[90]

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[87] Pfeiffer and Kramer, *Ber.*, **46**, 3655 (1913).

[88] Mathews and Williamson, *J. Am. Chem. Soc.*, **45**, 2574 (1923).

[89] Chattaway and Orton, *J. Chem. Soc.*, **75**, 1053 (1899).

[90] Rosenberg, *Vitamins*. Interscience, New York, 1945, p. 368.

J. REACTIONS INVOLVING OXYGEN

While gaseous oxygen shows a small amount of absorption in the near ultraviolet and visible parts of the spectrum, its intense absorption lies below 2000 Å. Except for the saturated aliphatic hydrocarbons nearly all organic molecules show absorption at longer wave lengths, and consequently, in mixtures of oxygen and organic compounds, the light is absorbed mainly by the latter.

In mixtures of oxygen and the simpler hydrocarbons, the reaction proceeds as it would in mixtures of ozone with these hydrocarbons. Ordinarily reaction is slow unless the temperature is raised, in which case chains and even branching chains leading to explosions may result. This type of reaction therefore does not lend itself conveniently to useful syntheses, even apart from the fact that to obtain significant intensities both the light source and the reaction vessel must be equipped with fluorite windows, and the air path must be reduced to an absolute minimum.

In general those organic molecules which form free radicals will react with oxygen under suitable irradiation. Numerous examples of this phenomenon could be cited. Thus biacetyl, paraldehyde, and ethyl alcohol all form compounds analogous to peroxides. The eventual products with ethyl alcohol are acetaldehyde and acetic acid. Most of these reactions are hard to control because the peroxides themselves are usually light sensitive. There seem to be no very useful reactions of this type although the matter might be worthy of some further investigation.

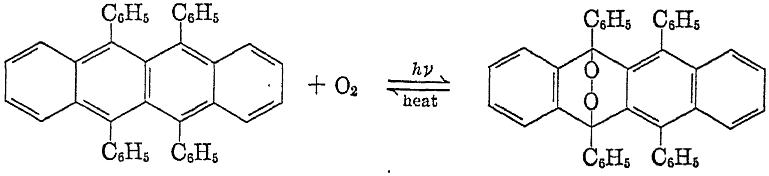
Unsaturated compounds usually react readily with oxygen photochemically, but once more the reaction is difficult to control. Thus ethylene gives carbon dioxide, carbon monoxide, formic acid, and probably some other products.[91] Toluene gives benzaldehyde, benzoic acid, and some products, such as acetic acid, which indicate a far reaching decomposition of the parent molecule.[92]

Aryl naphthacenes undergo an interesting photochemical reaction with oxygen to form compounds called photooxides. These compounds on standing or when heated decompose to give back the

[91] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1327 (1910).

[92] Kailan, *Monatsh.*, **40**, 445 (1920). Suida, *Ber.*, **45**, 2909 (1912); *Monatsh.*, **33**, 1255 (1912).

original hydrocarbon and free oxygen. The reaction of rubrene, a tetraphenylnaphthacene, is illustrated below.[93]



Rubrene

2. Chain Reactions Initiated by Light

From the preparative viewpoint the reactions of free radicals or atoms which are of the chain type are the most important because such reactions are usually fast, frequently give a high yield, and are suitable for preparing appreciable amounts of material. The discussion to follow is concerned with some of the important chain reactions in which the free atoms or radicals initiating the chain are generated by the action of light.

A. CHLORINATION

The usual photochlorination involves the dissociation of chlorine by light into free chlorine atoms which then initiate reaction chains either by substitution at a carbon-to-hydrogen bond or by addition to a carbon-to-carbon double bond. Chlorine in the gas phase or dissolved in a transparent liquid is quite readily dissociated so that the light source may be sunlight, diffuse daylight, or radiation from a Mazda lamp, carbon arc, or a mercury arc lamp. Although little critical investigation of the effect of wave length or light intensity has been done, the quantum yield must be very high for most photochlorinations and the reaction with simple hydrocarbons may even become explosive when high light intensity is used.

The mechanism for the photochlorination of paraffins is generally accepted as being the following:[94–96]

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[93] Moureu and Dufraisse, *Compt. rend.*, **182,** 1440 (1926). Dufraisse, *Bull. soc. chim.*, **2,** 1546 (1935); **3,** 1847, 1934 (1936).

[94] Brown, Kharasch, and Chao, *J. Am. Chem. Soc.*, **62,** 3435 (1940).

[95] Asinger, *Angew. Chem.*, **57,** 140 (1944).

[96] Hass, McBee, and Weber, *Ind. Eng. Chem.*, **28,** 333 (1936).

$$Cl_2 + h\nu \rightarrow 2\,Cl\cdot \qquad (31)$$

$$Cl\cdot + R_3CH \rightarrow R_3C\cdot + HCl \qquad (32)$$

$$R_3C\cdot + Cl_2 \rightarrow R_3CCl + Cl\cdot \qquad (33)$$

For this discussion R may be either an alkyl radical or hydrogen. Recombination of two chlorine atoms or union of two alkyl free radicals would represent chain-terminating steps. Likewise removal of chlorine atoms by reaction with a foreign substance would decrease the chain length. In agreement with this it is found that oxygen, phenols, and amines are inhibitors for photochlorination.[97–99]

The results obtained in the photochlorination of the paraffin hydrocarbons are very similar to those obtained in chlorinations in which free chlorine atoms are generated by heat or by peroxides. Thus Hass, McBee, and Weber[96] found that the same rules apply to photochlorination as for low-temperature thermal chlorination. Photochlorination yields all of the possible isomeric monochlorides, but the ease of replacement of hydrogen varies considerably depending on the location of the hydrogen and follows in the order of primary, secondary, and tertiary, with the tertiary hydrogens being replaced most easily. The relative difference in ease of substitution of hydrogen atoms is dependent on the temperature and also on whether the photochlorination is done in the gas phase or liquid phase. The effect of temperature is more marked in the liquid phase and as a result better control of the reaction can be had in liquid phase photochlorination.

For example liquid phase photochlorination of propane[96] at 30°C. yields a monochloropropane fraction which is 48% isopropyl chloride and 52% *n*-propyl chloride. When the reaction is carried out at −60°C., the product is 73% isopropyl chloride and 27% *n*-propyl chloride. Similarly isobutane[96] at 30° gives a mixture of 62.5% isobutyl chloride and 37.5% *tert*-butyl chloride, but at −55° the resulting mixture is 42% isobutyl chloride and 58% *tert*-butyl chloride.

In most cases photochlorination of a simple paraffin yields some of the dichlorinated product as well as more highly chlorinated material.

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[97] Leermakers and Dickinson, *J. Am. Chem. Soc.*, **54**, 4648 (1932). Dickinson and Carrico, *ibid.*, **56**, 1473 (1934).

[98] Müller and Schumacher, *Z. physik. chem.*, **B35**, 285 (1937).

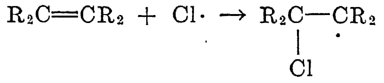
[99] Bloomfield, *J. Chem. Soc.*, **1944**, 114.

To obtain as high a yield of the monochlorinated product as possible it is customary to use an excess of the hydrocarbon.

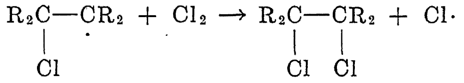
In the photochlorinations of propane and isobutane, yields of 80–95% of monochlorinated product can be obtained by using a threefold excess of hydrocarbon.[96] In the preparation of methyl chloride from methane, a sixteenfold excess of methane is employed to avoid simultaneous formation of methylene dichloride, chloroform, and carbon tetrachloride.[100] On the other hand, for compounds that react only slowly with chlorine it is usually advantageous to use a high chlorine concentration in order that the intermediate alkyl radical will have less opportunity to undergo side reactions.

Olefins add chlorine under conditions similar to those for substitution. The addition is a chain reaction and the mechanism ascribed to it is as follows:[97]

$$Cl_2 + h\nu \rightarrow 2\,Cl\cdot \qquad (34)$$



$$R_2C{=}CR_2 + Cl\cdot \rightarrow \underset{\text{Cl}}{\underset{|}{R_2C}}-\dot{C}R_2 \qquad (35)$$



$$\underset{\text{Cl}}{\underset{|}{R_2C}}-\dot{C}R_2 + Cl_2 \rightarrow \underset{\text{Cl}}{\underset{|}{R_2C}}-\underset{\text{Cl}}{\underset{|}{CR_2}} + Cl\cdot \qquad (36)$$

Since the addition of chlorine to olefins requires the same conditions as for substitution, the same considerations discussed under paraffin substitution apply here. Likewise it is not surprising that some substitution occurs simultaneously with addition. The extent to which substitution occurs depends largely on the nature of the olefin and with simple unsubstituted olefins, such as cyclohexene,[99] the per cent of substitution is quite appreciable. The photoaddition of chlorine to olefins is best employed for olefins which do not react readily in the dark or which are not readily substituted. The photochorinations of vinyl chloride,[101] ethylene dichloride,[98] and tetrachloroethylene[97] are examples.

The photochlorination of aromatic hydrocarbons may result in either addition or substitution or both. The photochlorination of benzene in either the liquid phase[102,103] or gas phase[104] yields mainly hexachlorocyclohexane, but when high chlorine concentrations and long exposure times are employed, the product is mainly dodecachlorocyclohexane. The formation of hexachlorocyclohexane probably proceeds by stepwise addition of chlorine to the double bonds present in benzene, although addition of chlorine to the dichlorocyclohexadiene first formed must occur exceedingly rapidly as no products of intermediate chlorination are ever found. The recent discovery that one of the isomers of hexachlorocyclohexane, called gammexane, is an excellent insecticide has made the photochlorination of benzene an important industrial reaction.[105] The procedure for large-scale production involves illumination of benzene with sunlight at room temperature in the presence of dilute base. In this way high yields of the isomeric hexachlorocyclohexanes are obtained of which 10–12% is the important isomer, gammexane.[105]

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[100] Padovani and Mazaldi, *Giorn. chim. ind. applicata*, **15**, 1 (1933); *Chem. Abstracts*, **27**, 3443 (1933).

[101] Schmitz and Schumacher, *Z. physik Chem.*, **B52**, 72 (1942).

In the case of alkyl benzenes photochlorination results mainly in substitution of the side chain and the reaction has been widely used for this purpose. The hydrogens attached to the carbon next to the ring are comparable in activity to a tertiary hydrogen in an aliphatic compound and are the first to be replaced. Although many aromatic compounds with chlorine in the alpha position have been prepared in this way, an evaluation of the photochemical reaction is difficult because under the conditions used simultaneous thermal chlorination occurs also. Thus in the usual procedure for chlorinating toluene,[106,107] an 85% yield of benzyl chloride is obtained by passing chlorine into an irradiated solution of the boiling hydrocarbon, but under these conditions an appreciable amount of chlorination will occur in the absence of light.

The ordinary procedure for liquid phase photochlorination is quite simple and necessitates only the addition of a source of light to the usual setup of glass apparatus. For compounds which are not liquid at the desired temperature a suitable solvent is used, such as carbon

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[102] Luther and Goldberg, *Z. physik. Chem.*, **56**, 43 (1906).

[103] Slator, *Z. physik. Chem.*, **45**, 540 (1903).

[104] Smith, Noyes and Hart, *J. Am. Chem. Soc.*, **55**, 4444 (1933).

[105] Slade, *Chem. Ind.*, **40**, 314 (1945); *Chem. Abstracts*, **40**, 2257 (1946).

[106] Gattermann and Wieland, *Laboratory Methods of Organic Chemistry.* Macmillan, London, 1938, p. 100.

[107] Asolkar and Guha, *J. Ind. Chem. Soc.*, **23**, 47 (1946).

tetrachloride or ethylene dichloride. Oxygen should be excluded from the system, and for most reactions it is sufficient merely to displace the air present with chlorine gas. Simple gas phase photochlorinations can be accomplished by passing chlorine into the vapors of the boiling liquid rather than into the liquid itself.[107] More specialized apparatus can be found described elsewhere.[108]

B. BROMINATION

The photochemical bromination of paraffins is similar in most respects to chlorination and the mechanism is thought to be the same.[109] The reaction can be carried out in solution or in the gas phase using either sunlight, Mazda lamps, carbon arc, or mercury arcs. Brominations proceed much more slowly than chlorinations and are of shorter chain length. This is undoubtedly due to the fact that substitution of a hydrogen by bromine is a less exothermic reaction than substitution by chlorine. This is of advantage in some respects because it allows greater control over the reaction.

Another advantage of photobromination is that the difference in ease of replacement between primary, secondary, and tertiary hydrogens is more marked than is the case with chlorinations. For example, the photobromination of isobutane[109] at room temperature yields only *tert*-butyl bromide. Under the same conditions neopentane, which has only primary hydrogens, does not react, although substitution of the primary hydrogens will take place at higher temperatures.[110] The bromination of a number of aliphatic hydrocarbons has been reported by Kharasch and his co-workers.[109,110]

The effect of oxygen on bromination is variable but in most cases small amounts of oxygen seem to accelerate the reaction. Kharasch and Berkman[111] explain this on the basis that small concentrations of oxygen can initiate chains by free radical formation in both chlorination and bromination, but that in chlorination the inhibiting effect of the chain-breaking reaction:

$$\mathrm{Cl\cdot} + \mathrm{O_2} \rightarrow \mathrm{ClO_2}$$

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[108] See Ellis and Wells, *Chemical Action of Ultraviolet Rays*. Reinhold, New York, 1941, pp. 528 and 530.

[109] Kharasch, Hered, and Mayo, *J. Org. Chem.*, **6,** 818, 705 (1941).

[110] Kharasch and Fineman, *J. Am. Chem. Soc.*, **63,** 2776 (1941).

[111] Kharasch and Berkman, *J. Org. Chem.*, **6,** 810 (1941).

outweighs the accelerating effect. A similar chain-breaking reaction can not occur with bromine. Large amounts of oxygen do inhibit bromination, though, and may cause direct oxidation of the reactant.[112]

The photoaddition of bromine to olefins is only useful for compounds which add bromine very slowly in the absence of light. For example, tetrachloroethylene[112] may be photobrominated in either the gas or liquid phase to give 1,2-dibromo-1,1,2,2-tetrachloroethane. Several molecules of bromine react per quantum absorbed, but the reaction does not go to completion, particularly if the temperature is raised to 100°C., because bromine atoms induce the dissociation of the dibromotetrachloroethane into bromine and tetrachloroethane.

Photobromination of aromatic compounds is for the most part analogous to photochlorination. Benzene[113] yields hexabromocyclohexane, and alkyl benzenes are substituted by bromine at the alpha position. Because photobromination occurs readily only with active hydrogens such as tertiary or alpha hydrogens, the photobromination of substituted benzenes is usually a more clean cut and versatile reaction than photochlorination. This is borne out by photobromination studies with variously substituted toluenes[114] and also with various alkyl aryl ketones.[115]

The procedure for photobromination differs from photochlorination mainly in that higher light intensities are needed to maintain an adequate rate of reaction because of the lower quantum yield. The procedure given below for the bromination of *p*-bromotoluene illustrates the usual method of photobromination of alkyl benzenes.

Preparation of p-Bromobenzyl Bromide.[116] 102 g. of *p*-bromotoluene (0.60 mole), in a three-necked flask fitted with dropping funnel, and reflux condenser, is heated to 120°C. and exposed to illumination from a 100-watt Mazda bulb placed as near the flask as possible. Bromine (102 g., 0.64 mole) is then added dropwise at a steady rate over a period of 3 hours while agitating the reaction mixture. When hydrogen bromide is no longer evolved, the reaction mixture is cooled and the solid mass is dried by filtration and washed with alcohol. The yield of *p*-bromobenzyl bromide, m.p. 61°, is 98–100 g. (66%). A slightly modified procedure with two equivalents of bromine gives high yields of *p*-bromobenzal dibromide.[117]

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[112] Williard and Daniels, *J. Am. Chem. Soc.*, **57**, 2240 (1935).

[113] Bowen and Williams, *Trans. Faraday Soc.*, **35**, 765 (1939).

[114] Sampey, Fawcett, and Morehead, *J. Am. Chem. Soc.*, **62**, 1839 (1940). Magee and Daniels, *ibid.*, **62**, 2825 (1940). Kindler and Bloas, *Ber.*, **77**, 585 (1944).

[115] Sampey and Hicks, *J. Am. Chem. Soc.*, **63**, 1098 (1941).

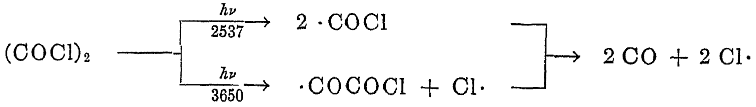
[116] Weizman and Patai, *J. Am. Chem. Soc.*, **68**, 150 (1946).

C. IODINATION

As might be expected, iodinations occur even more slowly than brominations. Substitution reactions do not seem to occur at all, and would not be expected at ordinary temperatures. Addition reactions are so slow as to be mainly of academic interest, although the various butenes will add iodine at low temperatures. The reason for this necessity of a low temperature undoubtedly resembles that for the necessity of not operating bromine addition reactions at high temperatures. Thus 1-butene will add iodine at −55°C. with visible light.[118]

D. CARBOXYLATION WITH OXALYL CHLORIDE

When the photodecomposition of oxalyl chloride is carried out in the presence of various aliphatic hydrocarbons, Kharasch and his co-workers, found that the hydrocarbons were converted to acid chlorides.[119] The way in which this occurs is thought to be as follows:



$$\mathrm{(COCl)_2} \begin{cases} \xrightarrow[2537]{h\nu} 2\cdot\mathrm{COCl} \\ \xrightarrow[3650]{h\nu} \cdot\mathrm{COCOCl} + \mathrm{Cl}\cdot \end{cases} \longrightarrow 2\,\mathrm{CO} + 2\,\mathrm{Cl}\cdot \qquad (37)$$

$$\mathrm{Cl}\cdot + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{HCl} \qquad (38)$$

$$\mathrm{R}\cdot + \mathrm{(COCl)_2} \rightarrow \mathrm{RCOCl} + \cdot\mathrm{COCl} \qquad (39)$$

As indicated in equation (1) the photodecomposition of oxalyl chloride appears to proceed differently at short wave lengths than at long, although the ultimate product is the same.

The carboxylation of cyclohexane, methylcyclohexane, chlorocyclohexane, cyclopentane, *n*-pentane, and isooctane by this method has been accomplished, although the yields are not always good and the unsymmetrical compounds yield mixtures.[119] Under the conditions tried, aromatic hydrocarbons and alkyl benzenes do not react. Certain unsaturated hydrocarbons, such as 1,1-diphenylethylene, styrene, α-methylstyrene, and 1-methylcyclohexene, react with oxalyl chloride by replacement of one of the hydrogens at the double bond with an acid chloride group, but this is apparently not a light-catalyzed reaction.[120]

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[117] See Blatt, *Organic Syntheses*. Coll. Vol. II, Wiley, New York, 1943, p. 89.

[118] Forbes and Nelson, *J. Am. Chem. Soc.*, **59**, 693 (1937).

[119] Kharasch and Brown, *J. Am. Chem. Soc.*, **62**, 454 (1940). Kharasch and Brown, *ibid.*, **64**, 329, 1621 (1942).

The formation of cyclohexanecarboxylic acid chloride by this method has preparative value and is described below:

Procedure for Cyclohexanecarboxylic Acid Chloride.[119] A mixture of cyclohexane (25.2 g., 0.3 mole) and oxalyl chloride (9.6 g., 0.075 mole) are placed in a 100-cc. flask of Pyrex glass fitted by means of a ground-glass joint to an efficient reflux condenser. The outlet of the condenser is connected to suitable traps for collecting carbon monoxide and hydrogen chloride. Illumination for the reaction is supplied by a 300-watt tungsten lamp placed immediately below the flask. The heat from the lamp is sufficient to keep the reaction mixture gently boiling. After 24 hours the reaction mixture is removed and on fractional distillation there is obtained 4.1 g. (85% of theoretical) of cyclohexanecarboxylic acid chloride (b.p. 99–101° at 52 mm.).

E. CHLOROSULFONATION

The conversion of aliphatic hydrocarbons to the corresponding alkyl sulfonyl chlorides is a reaction of some industrial importance.[121] The usual procedure for the reaction is to pass a mixture of equal volumes of sulfur dioxide and chlorine into an irradiated solution of the hydrocarbon in a suitable diluent such as carbon tetrachloride. Ordinary glass apparatus and sunlight suffices for the reaction but, presumably, better results are obtained using quartz apparatus and a mercury arc lamp.[122] The reaction is represented by the over-all equation:

$$RH + SO_2 + Cl_2 \overset{h\nu}{\quad} RSO_2Cl + HCl$$

Present evidence indicates that the reaction proceeds by the following mechanism:[121]

$$Cl_2 + h\nu \rightarrow 2\,Cl\cdot \tag{40}$$

$$Cl\cdot + RH \rightarrow R\cdot + HCl \tag{41}$$

$$\left\{\begin{array}{l} R\cdot + SO_2 \rightarrow RSO_2\cdot \\ R\cdot + Cl_2 \rightarrow RCl + Cl\cdot \end{array}\right. \tag{42}$$

$$RSO_2\cdot + Cl_2 \rightarrow RSO_2Cl + Cl\cdot \tag{43}$$

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[120] Kharasch, Kane and Brown, *J. Am. Chem. Soc.*, **64**, 333 (1942).

[121] Helberger, *Angew. Chem.*, **55**, 172 (1942). Schumacher and Stauff, *ibid.*, **55**, 341 (1942).

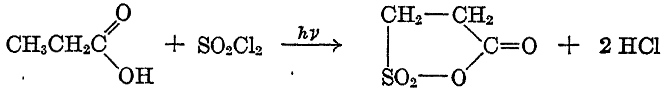
[122] Asinger, Schmidt, and Ebeneder, *Ber.*, **75**, 34 (1942). Asinger, Ebeneder, and Höck, *ibid.*, **75**, 42 (1942).

In accord with the above scheme alkyl chlorides are always found among the products of the reaction and also the ratio of isomers produced corresponds closely to that obtained in photochlorination.[122]

For example, chlorosulfonation of propane[122] gives an 85% yield of product which is approximately a 50–50 mixture of 1-propanesulfonyl chloride and 2-propanesulfanoyl chloride. Similarly *n*-butane[122] gives a mixture which consists of 67% 2-butanesulfonyl chloride and 33% 1-butanesulfonyl chloride.

Chlorosulfonation may be accomplished using sulfuryl chloride rather than a mixture of sulfur dioxide and chlorine, but in this case the presence of a catalyst, such as pyridine or quinoline, is necessary or the main product will be the alkyl chloride.[123] In this manner Kharasch and his co-workers have chlorosulfonated cyclohexane, ethylbenzene, *n*-heptane, *tert*-butylbenzene, and methylcyclohexane.[123] The alkyl bezenes, as would be expected, chlorosulfonate in the alpha position of the side chain.

Aliphatic acids also react with sulfuryl chloride, but in this case no added pyridine or quinoline is necessary.[124] With short-chain acids the product is the sulfoanhydride corresponding to beta substitution. The over-all equation for the reaction is illustrated below with propionic acid:



F. FORMATION OF THIO ETHERS AND MERCAPTANS

The addition of hydrogen sulfide and simple mercaptans to various olefins may be readily accomplished photochemically.[125,126] As the reaction is a rapid one giving high yields of a valuable product, it has considerable practical application. The main prerequisite is light of sufficiently short wave length (below 2800 Å.) to effect dissociation of the hydrogen-to-sulfur bond. The hydrogen atoms and —SR radicals can then initiate chains in the following ways:[125]

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[123] Kharasch and Read, *J. Am. Chem. Soc.*, **61**, 3089 (1939).

[124] Kharasch and Brown, *J. Am. Chem. Soc.*, **62**, 925 (1940). Kharasch, Chao and Brown, *ibid.*, **62**, 2393 (1940).

[125] Vaughan and Rust, *J. Org. Chem.*, **7**, 472 (1942).

[126] Rust and Vaughan, U. S. Pats. 2,392,294 and 2,392,295 (Jan. 1, 1946); *Chem. Abstracts*, **40**, 2453 (1947). Vaughan and Rust, U. S. Pats. 2,398,479 and 2,398,480 (April 16, 1946); *Chem. Abstracts*, **40**, 3765 (1947).

$$\mathrm{RSH} + h\nu \rightarrow \mathrm{RS}\cdot + \mathrm{H}\cdot \tag{44}$$

$$\begin{cases} \mathrm{H}\cdot + \mathrm{R'CH{=}CH_2} \rightarrow \mathrm{CH_3CHR'} \\ \mathrm{CH_3\dot{C}HR'} + \mathrm{RSH} \rightarrow \mathrm{CH_3CH_2R'} + \mathrm{RS}\cdot \end{cases} \tag{45}$$

or:

$$\mathrm{H}\cdot + \mathrm{HSR} \rightarrow \mathrm{H_2} + \mathrm{RS}\cdot$$

$$\mathrm{RS}\cdot + \mathrm{CH_2{=}CHR'} \rightarrow \mathrm{RSCH_2\dot{C}HR'} \tag{46}$$

$$\mathrm{RSCH_2\dot{C}HR'} + \mathrm{HSR} \rightarrow \mathrm{RSCH_2CH_2R'} + \mathrm{RS}\cdot \tag{47}$$

where R may be either a hydrogen or an alkyl group. Light of longer wave length can be employed if materials are added which dissociate to free radicals at these wave lengths. Thus by the addition of acetone light of about 3200 Å. may be used which in turn makes possible the use of Pyrex apparatus.[125]

The photochemical addition of hydrogen sulfide or mercaptans to olefins proceeds contrary to Markownikoff's rule, *i.e.*, the sulfur atom becomes attached to the carbon atom which has the larger number of hydrogen atoms. Thus, with hydrogen sulfide, butene-1 yields *n*-butyl mercaptan, propylene gives *n*-propyl mercaptan, and vinyl chloride gives β-chloroethylmercaptan.[125] Similarly *n*-propyl mercaptan and propylene react to give exclusively di-*n*-propyl sulfide.[125]

The experimental technique for the addition of hydrogen sulfide and mercaptans to olefins is relatively simple and is illustrated by the preparation given below for di-*n*-propyl sulfide.

Di-n-propyl Sulfide.[125] A quartz tube containing equimolar quantities of propylene and *n*-propyl mercaptan is cooled with liquid nitrogen, evacuated, and sealed. The tube is then warmed to 0°C. and held at that temperature for 6 minutes while being irradiated with the full radiation of a 400-watt mercury arc lamp placed 20 cm. from the tube. The tube is then chilled again, opened, and the unreacted propylene is allowed to evaporate. The remaining liquid is washed with 10% sodium hydroxide and then distilled giving a 96% yield of di-*n*-propyl sulfide; b.p. 141.5°; n_D^{20} 1.4480.

The reaction may be carried out in a similar fashion with Pyrex tubes, if a few drops of acetone are added to the reaction mixture.

G. ADDITION OF HYDROGEN BROMIDE TO OLEFINS

The addition of hydrogen bromide to olefins in the presence of ultraviolet light has been investigated by Vaughan, Rust, and Evans[127] who found that the addition proceeded rapidly and in high yields but in a manner contrary to Markownikoff's rule. In every case the bromine becomes attached to the carbon atom of the double bond having the greater number of hydrogen atoms. In this respect the effect of ultraviolet light closely resembles the "peroxide effect" which Kharasch, Mayo, and their co-workers[128] have studied so extensively. Undoubtedly both reactions proceed by a chain process involving bromine atoms.

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[127] Vaughan, Rust, and Evans, *J. Org. Chem.*, **7**, 477 (1942).

The ultaviolet light employed in the addition of hydrogen bromide must be sufficiently short (below 2900 Å.) to cause dissociation of the hydrogen bromide, and the reaction scheme is thought to be:[127]

$$\mathrm{HBr} + h\nu \rightarrow \mathrm{H}\cdot + \mathrm{Br}\cdot \tag{48}$$

$$\mathrm{RCH{=}CH_2} + \mathrm{Br}\cdot \rightarrow \mathrm{R}\underset{\cdot}{\mathrm{C}}\mathrm{HCH_2Br} \tag{49}$$

$$\mathrm{R}\underset{\cdot}{\mathrm{C}}\mathrm{HCH_2Br} + \mathrm{HBr} \rightarrow \mathrm{RCH_2CH_2Br} + \mathrm{Br}\cdot \tag{50}$$

Again, as with sulfide addition, light of longer wave length may be used if photodecomposable substances such as acetone, acetaldehyde, or lead tetraethyl are added.[127]

The photochemical addition of hydrogen bromide to olefins may be done in either the gas phase or the liquid phase. In the gas phase hydrogen bromide has been added to ethylene, propylene, butene-1, and isobutene, whereas in the liquid phase it has been added to butene-1, propylene, allyl bromide, and diallyl.[127] The reactions are complete in a few minutes and give almost quantitative yields. The experimental technique is very similar to that used in the addition of sulfides to olefins.

H. ADDITION OF POLYHALOGEN COMPOUNDS

Various polyhalogen compounds, including carbon tetrachloride, carbon tetrabromide, and bromotrichloromethane have been added to olefins in the presence of ultraviolet light.[129,130] The reaction probably proceeds as follows:

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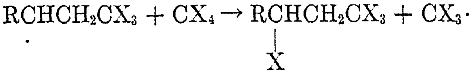
[128] Mayo and Walling, *Chem. Revs.*, **27**, 351 (1940).

[129] Kharasch, Jensen, and Urry, *J. Am. Chem. Soc.*, **69**, 1100 (1947); *ibid.*, **68**, 154 (1946).

[130] Kharasch, Reinmuth, and Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947). See also Sommer, Pietrusza, and Whitmore, *ibid.*, **69**, 188 (1947).

$$CX_4 + h\nu \rightarrow CX_3\cdot + X\cdot \qquad (51)$$

$$RCH{=}CH_2 + CX_3\cdot \rightarrow R\underset{\cdot}{C}HCH_2CX_3 \qquad (52)$$



$$R\underset{\cdot}{C}HCH_2CX_3 + CX_4 \rightarrow R\underset{\underset{X}{|}}{C}HCH_2CX_3 + CX_3\cdot \qquad (53)$$

The olefins utilized in this reaction have been octene-1, styrene, ethylene, and propylene.[129,130]

The additions proceed readily at low temperatures and for the most part high yields of the desired product are obtained. The wave length of light necessary for dissociation of the polyhalogen compounds varies from 2800 Å. for carbon tetrachloride to 3500 Å. for carbon tetrabromide. As can be seen from the proposed mechanism, the intermediate free alkyl radical might react with an olefin molecule to initiate polymerization instead of reacting with a polyhalogen molecule. In order to minimize such polymerization a two- or threefold excess of polyhalogen compound is used.[129,130]

VII. CONCLUSIONS

The use of photochemistry as an aid to the synthetic organic chemist demands much more careful study. The numerous random and uncoordinated results reported in the literature indicate that useful reactions could be found in large numbers.

Since many organic molecules absorb over a wide spectral range, many light sources are available. Some of these are cheap and reliable and for many reactions Pyrex vessels and ordinary high-power light bulbs are adequate. However, just as with the more customary methods of organic chemistry, there are often side reactions which are troublesome. *Occasionally*, but by no means always, the photochemical approach leads to the desired result with less difficulty than the usual methods. Probably the photochemical method should be tried oftener when other methods are cumbersome or fail. In any case enough systematic studies should be made so that predictions of the courses of reactions can be made. In this respect organic photochemistry is still in its swaddling clothes.

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Noyes and Leighton, *The Photochemistry of Gases.* Reinhold, New York, 1941.

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ELECTROLYTIC REACTIONS

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I. INTRODUCTION

Study of electrolytic reactions of organic compounds began soon after the discovery of the electrolysis of water by Nicholson and Carlisle in 1800. They were not used in syntheses, however, until after 1847 when Kolbe discovered that aliphatic hydrocarbons could be prepared by the electrolysis of the salts of aliphatic acids. The field has expanded greatly since that time and it is now possible to carry out syntheses by electrolytic reduction, oxidation, cathodic coupling, anodic coupling, and substitution.

In the present chapter there will be given a brief résumé of the general theory, followed by a description of the equipment and its operation. There will then be a discussion, from a theoretical and practical point of view, of reactions at the cathode, reactions at the anode and, finally, of reactions in which inorganic intermediates are formed. The various techniques are illustrated by a number of procedures which were selected so that their yields are comparable to those by any other method.

II. GENERAL THEORY

1. Definitions

If pieces of platinum or other unattackable material dipping into a solution of a conductor, such as an acid, base, or salt, are connected to the two poles of a suitable source of direct current, current will flow through the solution provided that the voltage of the source of direct current is high enough to overcome the resistance of the circuit.

The solution through which the current flows is called the *electrolyte* and the passage of current through the solution is called *electrolysis*. The terminals of the connections to the poles are called *electrodes*. At one of the electrodes positively charged ions receive electrons. The electrode which supplies electrons is called the negative electrode or *cathode*. At the other electrode negatively charged ions give up electrons. The electrode which receives electrons from the solution is called the positive electrode or *anode*.

Example:

At cathode	At anode
$H^+ + e. \rightarrow H$	$OH^- \rightarrow e + OH$
$R_4N^+ + e \rightarrow R_4N$	$RCOO^- \rightarrow e + RCOO$

If the cathode is separated from the anode by a porous barrier, called a diaphragm, the electrolyte on the cathode side is called the *catholyte* and that on the anode side, the *anolyte*.

The quantity of electricity which flows through the solution is measured in coulombs and the strength of the current, in amperes. A current has the strength of 1 *ampere* when one coulomb passes per second.

The quantities of materials formed at the electrodes are related to the amount of current which passes through the solution. This relationship was first expressed by *Faraday in two laws* which are as follows: (*1*) the quantities of substances set free at the electrodes are directly proportional to the quantity of electricity which passes through the solution; and (*2*) the same quantity of electricity sets free the same number of equivalents of substances at the electrodes. One equivalent weight of material will be liberated at an electrode by the passage of slightly more than 96,500 coulombs of electricity or *one Faraday*. The Faraday may also be defined in terms of the strength of current flowing per unit of time or the ampere hour—one ampere flowing for one hour. One Faraday is the equivalent of 26.8 ampere hours.

The concentration of the material formed at an electrode will depend on the *current density* (abbreviation c.d.) or number of amperes flowing into a unit electrode surface. It is usually expressed in amperes per square centimeter or decimeter except in industrial operations where the units ampere per square inch or square foot are used.

Another factor related to the rate of formation of materials at the electrodes is the *current concentration* or number of amperes flowing through a given volume of solution.

Theoretically a given quantity of current should produce an equivalent amount of product at an electrode. Due to several factors, *i.e.*, competing reactions, etc., this usually does not occur. The quantity of material actually formed at an electrode divided by the amount which should have been formed is called the *current efficiency.*

The container with solution and electrodes is called the cell.

Glossary

Direct current	unidirectional current
Voltage	electrical pressure
Electrode	connection of source of current to electrolyte
Anode	pole of electrolytic cell at which oxidation takes place
Cathode	pole of electrolytic cell at which reduction takes place
Electrolyte	solution containing electrolytic conductor
Anolyte	electrolyte in anode compartment
Catholyte	electrolyte in cathode compartment
Conductor	carrier of current
Coulomb	unit of quantity of current
Ampere	unit of strength of current
Faraday	96,500 coulombs or 26.8 ampere hours
Ampere hour	a current of one ampere flowing for one hour
Current density	number of amperes flowing into a unit of surface
Current concentration	number of amperes flowing through a unit of volume
Current efficiency	actual amount of product divided by theoretical amount based on quantity of current
Cell	container with solution and electrodes

2. Mechanism of Electrolysis

A. CONDUCTANCE

In carrying out electrolyses the nature of the conductor in the solution and also the nature of the solvent itself are of importance.[1] The solutions should, if possible, be of such nature that there is present a plentiful supply of ions to receive electrons from the cathode or to give them up at the anode. If the supply of ions is insufficient, high voltages will be necessary to force current through the solution due to its resistance. It is, therefore, desirable to use highly ionized acids, bases, and salts. Too high a concentration of the conductor will repress ionization and hence increase the resistance of the solu-

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[1] Shedlovsky, in Weissberger, ed., *Physical Methods of Organic Chemistry.* Interscience, New York.

The most widely available solvent which is also one of the best media for promotion of ionization is water. It is possible, however, to carry out electrolyses successfully in nonaqueous solvents. The viscosity of the solvent is important in electrolysis. A low viscosity favors rapid migration of ions. An increase in the temperature will not only lower the viscosity, but will increase the conductance to a maximum after which it will decrease with further increase in temperature.

B. REACTIONS AT ELECTRODES

It was stated previously that when direct current is allowed to pass through a solution positively charged ions take up electrons from the cathode while negatively charged ions give up electrons to the anode. As there are often several ions present in a solution, it is necessary to know which ones will be discharged. It was previously indicated that a definite potential must be applied across the electrodes of a cell before current will pass. Part of the resistance of the cell is due to the work necessary to discharge ions. The amount of work varies with the particular ion. The ion the discharge of which requires the least work will be neutralized first. The discharge potential of the electrolyte may be regarded as the sum of the discharge potentials at the cathode and at the anode. An idea of the ease of discharge of some of the more common ions may be gained from Table I.

The potentials express equilibria between the substance and its ions in molal concentration. Negative potentials indicate a tendency for the metal to lose an electron and become an ion while the reverse is true of positive potentials. It may be seen, then that H^+ will take up an electron much more easily than Na^+ and will, therefore, be discharged in preference to Na^+. At the anode where the process is reversed I^- will lose an electron much more readily than Cl^- and will, therefore, be discharged in preference to Cl^-. The values shown in Table I will vary with the concentration of the ion. For example, OH^- in an alkaline solution will be discharged more readily than in acid solution.

When aqueous solutions of alkali and alkaline earth salts are electrolyzed, the product at the cathode is hydrogen from the water. The region next to the cathode becomes alkaline due to the formation of hydroxyl ion. Most of the ions of the common metals are sufficiently electropositive to take up electrons at the cathode and the metals will, therefore, be deposited. Electrons may also be absorbed by organic compounds which may or may not be ionized. In a few cases the organic compound is in equilibrium with its reduced form and its reduction potential will depend on the concentrations of both forms. The better known systems of this type are: quinone–hydroquinone, nitrosobenzene–phenylhydroxylamine, and azobenzene–hydrazobenzene.

TABLE I[2]

Equilibrium — Electrolytic Potentials at 25°C.

Cation	Potential, volts	Anion	Potential, volts
K, K^+	−2.96	O_2, OH^-	+0.40
Na, Na^+	−2.72	I_2, I^-	+0.54
H_2, H^+	0.00	Br_2, Br^-	+1.07
		Cl_2, Cl^-	+1.36

At unattackable anodes OH^- ions are discharged in preference to most of the common inorganic anions not shown in Table I except at high concentrations and H^+ ion is formed in the region near the anode. Again, certain organic anions may discharge at the anode in preference to OH^-.

C. POLARIZATION AND OVERVOLTAGE

When gases are produced in the electrolysis of aqueous solutions at unattackable electrodes resistance in the form of a back electromotive force develops, possibly on account of the fact that the gases are not liberated immediately or that the ions are not discharged.[3] In either case the cell acts as if it were a battery in opposition to the applied electromotive force. The phenomenon described is called *polarization*. The amount of back electromotive force depends on the electrode materials. It will require a higher voltage for passage of current between two electrodes of smooth platinum, for example, than between electrodes of platinum black. As was stated earlier, the back electromotive force may be regarded as being the sum of the voltages of two half cells and that a certain minimum voltage is necessary before the ions themselves would be discharged. The voltage in excess of the minimum voltage or equilibrium potential (see Table I) for the discharge of the ion is called the *overvoltage*. Hydrogen and oxygen overvoltages are those of most interest in organic reactions, but other gases such as the halogens also have overvoltages. Overvoltage increases with rise in current density and decreases with rise in temperature.

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[2] Creighton and Koehler, *Principles and Applications of Electrochemistry.* Vol. II, Wiley, New York, 1944, p. 38.

The exact nature of overvoltage is not known, but many theories have been proposed to account for it. Hydrogen overvoltage, for example, has been explained by assuming the formation of hydrides which would generate a back electromotive force. It has also been explained by assuming that high concentrations of atomic hydrogen are present on the cathode surface. The hydrogen would tend to lose an electron to the cathode thus developing a back electromotive force. Other theories assume that the hydrogen ion is discharged with difficulty and that the transfer of a proton from the solution to the electrode requires energy. The cathodes of high hydrogen overvoltage are the metals with low melting points such as mercury, cadmium, zinc, lead, and tin. Nickel, smooth platinum, and platinum black have low hydrogen overvoltages, platinum black having the lowest.

There are not many metals which are unattackable as anodes and of those most commonly used, smooth platinum and lead oxide have very high oxygen overvoltages. Platinum black has the lowest oxygen overvoltage.

Overvoltage is not only directly important in the reduction and oxidation of organic compounds—as will be shown later—but also in carrying out reductions in alkaline solution at a mercury cathode and in chlorination.

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[3] Glasstone, *An Introduction to Electrochemistry*. Van Nostrand, New York, 1942, Chapter 13.

Hydrogen will normally be deposited at the cathode in preference to sodium or potassium. If, however, electrolyses of sodium or potassium salts are carried out with a mercury cathode, sodium and potassium will be discharged until the mercury is saturated due to prevention of discharge of hydrogen by its high overvoltage.

In carrying out electrolyses of chloride solutions OH^- would normally be discharged before Cl^-. In neutral or acid solutions if the concentration of chloride ion is kept high, the discharge of OH^- will not take place on account of the high oxygen overvoltage at the anode.

D. DEPOLARIZATION

Any substance which reduces polarization is called a *depolarizer*. Two mechanisms by which depolarizers may function are by reaction with the substance formed at the electrode before it is liberated or by accepting an electron from or donating an electron to an electrode. In reductions the cathode potential may be maintained below that required for hydrogen evolution if the atomic hydrogen before its release reacts with a compound or if the compound accepts electrons from the cathode.[4] The anode potential may be maintained below that for oxygen evolution if before its discharge atomic oxygen reacts with a compound or the compound donates an electron to the anode.[5,6] Thus in many, but not in all, cases of electrolytic reduction and oxidation of organic compounds the compound behaves as a depolarizer.

Leslie and Butler[7] point out that pyridine is reduced to piperidine at potentials at or near that of hydrogen evolution at a lead cathode, and that it is probable that the active reducing agent in this case is atomic hydrogen. On the other hand, nitrobenzene behaves as a true depolarizer and lowers the cathode potential. They propose the following mechanism for the first step in the reduction of nitrobenzene to phenylhydroxylamine:

$$C_6H_5NO_2 + 2\,e \rightarrow C_6H_5NO_2^{--} + 2\,H^+ \rightarrow C_6H_5NO + H_2O$$

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[4] O. H. Müller, in Weissberger, ed., *Physical Methods of Organic Chemistry*. Interscience, New York.

[5] Butler, *Electrocapillarity*. Methuen, London, 1940, Chapter 8.

[6] Glasstone, *Introduction to Electrochemistry*. Van Nostrand, New York, 1942, Chapter 15.

[7] Leslie and Butler, *Trans. Faraday Soc.*, **32**, 989 (1936).

Nitrobenzene accepts two electrons from the cathode to form a negatively charged ion which is neutralized by the hydrogen ions of the solution to form nitrosobenzene and water.

The electrode potential will remain below that for liberation of the gases as long as sufficient depolarizer is present at the electrode surface and the rate of production of atomic hydrogen is not faster than its absorption by the depolarizer. The factor which controls the rate is the current density.

In certain cases the actual potential or overvoltage at which reduction or oxidation takes place will influence the type of product formed. When nitrobenzene is reduced in acid solution at a platinum black cathode at very low potentials intermediate products such as *p*-aminophenol are found, while at higher potentials aniline is the main product.[8] Aniline is also the main product at a cathode of high hydrogen overvoltage.[9] In general, the higher the overvoltage, the more complete will be the reduction or oxidation. Not only does a high overvoltage favor completeness of reduction or oxidation, but it also increases the rate. Compounds such as caffeine are not reduced at a smooth platinum cathode but are readily reduced at a lead cathode.[10] Similar conditions obtain in the reduction of α,α'-dithiobispropionic acid, $CH_3CH(COOH)SS(HOOC)CHCH_3$, to α-mercaptopropionic acid, $CH_3CHSHCOOH$.[11] Overvoltage will be discussed further in later sections. Exactly why a high overvoltage favors completeness and increase of rate of a reaction is not known.[6]

E. CATALYSIS

At certain cathodes of low hydrogen overvoltage the organic compound apparently reacts with hydrogen after it has been liberated as a molecule. Mesityl oxide, $(CH_3)_2C = CHCOCH_3$, undergoes reduction to a bimolecular compound at cathodes of high hydrogen overvoltage, while at a freshly electrodeposited copper cathode the main product is methyl isobutyl ketone, the type of compound which would be expected in catalytic hydrogenation.[12] When sorbic acid, $CH_3CH = CHCH = CHCOOH$, is subjected to reduction at cathodes of high hydrogen overvoltage, 1,2 or 1,4 addition of hydrogen

[8] Haber, *Z. Elektrochem.*, **4**, 506 (1898).

[9] Elbs, *Chem.-Ztg.*, **17**, 209 (1893).

[10] Tafel, *Ber.*, **33**, 2209 (1900).

[11] Larsson, *Svensk Kem. Tid.*, **40**, 150 (1928).

[12] Law, *J. Chem. Soc.*, **101**, 1544 (1912).

takes place at the double bonds or a bimolecular reduction product is formed. At a cathode of platinum black complete saturation of the double bonds results and the main product is caproic acid.[13] Copper and platinum black are known to be catalysts for hydrogenation.

In oxidation it has been found that platinum black, an anode of low oxygen overvoltage, carried the oxidation of methyl alcohol completely to carbon dioxide and water.[14]

3. Quantity of Current Required in Electrochemical Reactions

It is sometimes desirable to carry out an operation with one, two, or more reactive groups in a molecule. For example, if *p*-nitrobenzoic acid is reduced in sulfuric acid solution at a lead cathode with an unlimited amount of current, *p*-aminobenzyl alcohol will be the main product. If *p*-aminobenzoic acid is the desired product, just 6 Faradays of electricity should be allowed to pass. A simple method for calculating the theoretical amount of current necessary for the reduction of a given quantity of compound and the number of hours necessary for it is shown below:

$$\frac{\text{M.W.}}{w} = \frac{6 \times 26.8}{n}$$

$$h = \frac{n}{i}$$

where M.W. is the molecular weight of *p*-nitrobenzoic acid, w is the weight of *p*-nitrobenzoic acid, 26.8 is the number of ampere hours in one Faraday, n is the number of ampere hours required, i is the current in amperes, and h is the number of hours required.

III. APPARATUS AND GENERAL PROCEDURE

1. Equipment

All electrochemical preparations are carried out with direct current supplied at voltages up to 16 volts except when certain nonaqueous solutions are used. In these cases voltages up to about 100 volts may be necessary.

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[13] Wilson, *Trans. Electrochem. Soc.*, **75**, 353 (1939).

[14] Glasstone and Hickling, *Electrolytic Oxidation and Reduction.* Chapman & Hall, London, 1935, p. 337.

The source of supply may be a generator, a storage battery, or possibly rectified alternating current. Rectified current seems to have been used very little in electro-organic chemistry possibly on account of its fluctuation. The ordinary house current at 110 volts d.c. controlled by a slidewire resistance of 17 ohms and having a maximum current rating of 6.2 amperes should be satisfactory for electrolysis requiring higher voltages. It may also be used for electrolysis at low voltage when controlled by a lamp bank resistance as shown in Figure 1. The lamps are in parallel and varying amperages may be maintained by using lamps of different sizes. For maintaining amperages of about 5 amperes, a 600-watt, cone-type heating element may be used to replace several lamps. The most convenient source of low voltage direct current is one with variable voltage. The following slidewire resistances should be satisfactory for maintaining the desired amperages: 180 ohms with a maximum current rating of 1.6 amperes, 44 ohms with a maximum current rating of 3.1 amperes, 17 ohms with a maximum current rating of 6.2 amperes, and 28 ohms with a maximum rating of 12 amperes. At the beginning of a run the rheostat should always be set so that its resistance is at a maximum and the maximum current rating should not be exceeded.

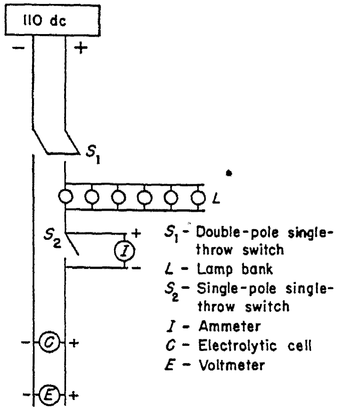

Fig. 1. Wiring diagram with 110 d.c. source and lamp bank.

The current is measured with an ammeter, which should be bypassed by a shunt when not in use. For general use an ammeter with ranges of 0 to 3, 0 to 15, and 0 to 30 amperes will be satisfactory. A convenient shunt is a single-pole, single-throw switch which is opened when the ammeter is to be read (see Fig. 1). Currents on a laboratory scale are usually not greater than 10 amp.

If it is desired to measure the number of ampere hours which have passed through the cell during a run, a *copper coulometer* may be placed in the circuit. The coulometer is made by placing a copper sheet cathode between two thick copper sheet anodes in a small rectangular battery jar containing a solution of 125 g. per liter of $CuSO_4 \cdot 5H_2O$, 50 g. of sulfuric acid, and 50 g. of ethyl alcohol. The dry cathode is weighed before and after the run. The number of ampere hours may be calculated as follows from the weight of copper deposited:

$$\frac{\text{equiv. wt. of Cu}}{\text{wt. of Cu}} = \frac{26.8 \text{ amp. hr.}}{\text{no. of amp. hr.}}$$

The voltage may be ascertained by connecting the terminals of a voltmeter to the anode and cathode of the electrolytic cell (see Fig. 1). A voltmeter with ranges of 0 to 3, 0 to 15, and 0 to 150 volts will be suitable.

Small battery clamps may be used conveniently for connecting the lead wires from the source of current to the anode and cathode. The use of a double-pole switch connected directly to the source of current is recommended for turning the current on and off.

Polarity Test. If the polarity of the current source is not known, it may be determined by turning on a small current and touching a piece of filter paper soaked with a sodium chloride solution containing a little phenolphthalein to the terminals of the lead wires. The region of the paper in the vicinity of the negative pole or cathode will turn pink.

A. ELECTRODES

Electrodes may be solid or porous in the shape of round or rectangular bars or sheets, gauze, or liquid—as in the case of mercury. Single pieces of metal may be used or several pieces connected in parallel.

Solid electrodes should have tabs to which the lead wires are connected. The tabs should extend well above the electrolytic bath or be bent away from the cell so that fumes will not reach the lead wires and cause some of their metal to corrode and fall into the bath (see Fig. 2).

A convenient way of preventing fumes from reaching the connections is to insert the tabs through holes cut in rubber stoppers which are fitted into the cell. The stoppers are equipped with reflux condensers or tubes which extend above the tops of the tabs to carry away the gases which are formed during the electrolysis (see Fig. 3).

If wire tabs are to be used, they may be sealed into glass tubes with wax and the glass tube inserted in the rubber stopper. When a platinum wire is used, it is sealed into a glass tube which is filled with mercury as a conductor. Connections to mercury cathodes are made in this manner, with a small platinum wire submerged. Platinum wires may be attached to platinum sheets by the blow of a hammer on the wire at the places where it and the sheet have been heated to redness by a blast lamp.

Cathodes. The following metals have given good results as cathodes in preparative work: copper, zinc, cadmium, mercury, tin, lead, nickel, and platinum. With the exception of mercury the cathodes have been used in the form of bars or sheets. Copper and nickel have also been used in the form of gauze. In addition to the metals carbon and graphite have been successful cathodes. Copper, nickel, lead, and platinum are available commercially in the form of sheets; copper, nickel, and platinum in the form of gauze; and cadmium, zinc, lead, and tin in the form of sticks. Carbon or graphite is obtainable as sticks or large bars which may be sawed to shape. The metals should be the purest obtainable. It is possible that one form of the lead sheet or stick will give better results than the other form (see section on factors controlling reduction, IV-1-A).

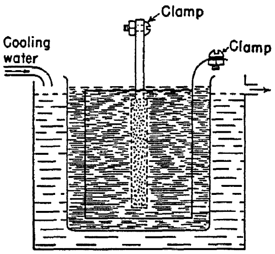

Fig. 2. Cell with connections to electrodes.

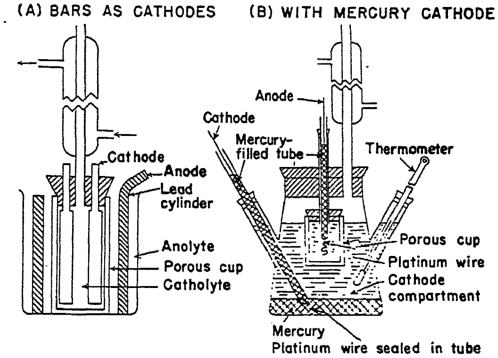

Fig. 3. Apparatus for electrolytic reductions.

In addition to the metals themselves specially prepared cathodes have been found advantageous. Among these electroplated metals are important. A suitable metal for receiving the electroplate is made the cathode in a bath containing a salt of the metal to be plated. The anode may be made of the metal to be plated or may be unattackable. When the current is turned on, the metal ions discharge at the cathode. A convenient form of cathode is a sheet cut so that a tab extends well above the solution. In order to obtain a plate of uniform thickness the cathode is placed between two anodes which are equidistant from it. The composition of the bath is important, also the current density at the cathode and the temperature. The plate should extend a few centimeters up the tab and the exposed metal which supports the plate should be covered by some impervious material such as a rubber stopper, as shown in Figure 3. It is recommended that the electroplate be about 1/16 inch in thickness so that it will be impervious and last for a number of anodizations (see page 171) and runs.

Copper electroplated on copper,[15] lead electrodeposited on lead[15,16] and on copper,[17] and platinum black on copper[18] have been used as cathodes. Copper may be conveniently plated from a sulfate bath. The following conditions are suggested by Blum and Hogaboom[19]: copper anodes, bath containing 200 g. per liter of $CuSO_4 \cdot 5H_2O$ and 50 g. per liter of sulfuric acid, and a cathodic current density of 0.02 to 0.04 amp. per cm.^{2}. The temperature should be about 25–50°C. The cathode of lead on lead was electroplated from a bath of potassium plumbate[16] and from a hot solution of lead chloride and hydrochloric acid containing hydroxylamine hydrochloride,[15] while the cathode of lead on copper was plated from a solution of lead perchlorate.[20] Excellent results have been obtained with a bath containing 11.8% lead perchlorate[21] with 4 to 6% excess perchloric acid. The perchlorate is made up by pouring a suspension of lead carbonate slowly into dilute perchloric acid. In order to obtain a fine-grained deposit 0.05% of peptone is added to the bath. A copper cathode is placed between two lead anodes. The distance between cathode and anode is about one inch. The copper cathode should be cleaned with sulfuric acid and dilute nitric acid. The cathodic current density is 0.02 amp. per cm.^{2}. The lead electroplate is obtained in oriented condition. The corners of the cubic crystals face the solution. A method for electroplating platinum black has been described in a previous volume of this series.[22]

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[15] Bruckner and Kardos, *Ann.*, **518**, 226 (1935).

[16] Fichter and Stein, *Helv. Chim. Acta*, **12**, 821 (1929).

[17] Swann and Lucker, *Trans. Electrochem. Soc.*, **75**, 411 (1939).

[18] Itomi, *Mem. Coll. Sci. Kyoto Imp. Univ.*, **A13**, 311 (1930).

[19] Blum and Hogaboom, *Principles of Electroplating and Electroforming.* 2nd ed., McGraw-Hill, New York, 1930, p. 216.

[20] Mathers, *Trans. Am. Electrochem. Soc.*, **23**, 159 (1913).

[21] Mauterer, Chemical Engineering Senior Project, University of Illinois, 1947.

In addition to specially prepared pure metal cathodes alloys have also given good results. Those which are obtainable in the form of gauze or sheet are Monel metal and phosphor bronze.[23, 24] Amalgamated nickel[25] and one type of amalgamated zinc[26] are prepared by allowing the metals to stand in solutions of mercuric chloride. Two methods have been used for making amalgamated lead: by rubbing mercury into a lead sheet[27] and by allowing a lead sheet to stand in a mercuric chloride solution.[28] As in the case of pure metals alloys have also been prepared by electrodeposition. Copper gauze has been tinned.[29] The thickness of the tin plate is not given. Tin may be electroplated on the copper from a solution of stannous sulfate.[30] A zinc amalgam containing more mercury than that previously described may be prepared by electrodepositing zinc into a mercury cathode from a solution of zinc sulfate until the cathode is solid.[31]

In this laboratory studies have been carried out to determine the influence of the cathode material on the electrolytic reduction of organic compounds. The following cathodes have been used in acid and alkaline solutions: cadmium, zinc, lead, mercury, tin, bismuth, copper, nickel, cobalt, and iron. In acid solution only aluminum has been used and in alkaline solution only chromium, tungsten, molybdenum, and magnesium. The influence of the temperature at which a low-melting metal is cast on its properties as a cathode has also been studied. Cadmium, zinc, tin, and lead have been cast in molds at room temperature and at 50°C. below their melting points. Experience in casting is necessary for this work and it is recommended that a metallurgist be consulted. Wherever possible, metals having a purity of 99.95% or higher have been used. Cadmium, zinc, lead, and tin have been used in the form of bars recast as stated before. Tungsten, copper, and magnesium have been obtained in the form of rods, molybdenum in sheets, and nickel in thick plates which are sawed to shape. Bismuth, cobalt, and chromium have been used in the form of electroplates on copper. Bismuth is readily plated from a perchlorate bath.[32] Bismuth anodes are used with a copper cathode. The bath is a saturated solution of bismuth perchlorate, 10.4 g. of 72% perchloric acid, and 4.6 g. of bismuth trioxide per 100 cc. of solution. The cathodic current density[33] was 0.015 to 0.018 amp. per cm.^{2}. Mild stirring of the bath is recommended. The electroplated cathode is used because bismuth sticks are too brittle. Chromium may be deposited on copper from a bath containing 250 g. per liter of chromic acid and 1.25 to 2.5 g. per liter of sulfuric acid.[34] The copper cathode is placed between two anodes of sheet lead. The cathodic current density is 0.1 to 0.3 amp. per cm.^{2} and the temperature, 45 to 55°C. Cobalt is plated from a bath of the sulfate, sodium chloride, and boric acid.[35] Commercial cobalt anodes were used with a copper cathode. The cathodic current density was 0.048 amp. per cm.^{2}. 2 to 5 cc. of hydrogen peroxide[36] was added to the bath every two or three hours to react with the hydrogen at the cathode and thus prevent the formation of cobalt hydride.

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[22] Michaelis, in Weissberger, ed., *Physical Methods of Organic Chemistry.* Interscience, New York, 1946, Chapter 22, *Potentiometry*, p. 1059.

[23] McKee and Brockman, *Trans. Electrochem. Soc.*, 62, 203 (1932).

[24] McKee and Gerastopolou, *ibid.*, 68, 329 (1935).

[25] Bougault, Cattelain, and Chabrier, *Compt. rend.*, 208, 193 (1939).

[26] Shima, *Mem. Coll. Sci. Kyoto Imp. Univ.*, A13, 315 (1930).

[27] Creighton, U. S. Pat. 1,990,582 (1935).

[28] Oroshnik and Spoerri, *J. Am. Chem. Soc.*, 63, 3338 (1941).

[29] Backer, *Rec. trav. chim.*, 31, 1 (1912).

[30] Pine, *Trans. Electrochem. Soc.*, 80, 631 (1941).

[31] Sakurai, *Bull. Chem. Soc. Japan*, 7, 155 (1932).

Anodes. The number of metals which may be used as anodes is limited by the fact that most of them are easily corroded. Those which have given good results in preparative work are smooth platinum and brown lead oxide. Iron and nickel have been used in alkali only. Carbon or graphite have been used in acid and alkali, but will be attacked to some extent to form oxides and other products. Platinum electrodes will be attacked slightly by halogens, and the lead oxide, markedly. If ammonium salts or amines are present platinum and nickel will be attacked. Lead will be attacked by solutions of certain acids among which are the organic acids.

The brown lead oxide mentioned above is prepared very simply by making lead the anode in a dilute sulfuric acid solution.

B. ELECTROLYTES

The electrolyte may contain any of a large number of compounds which will form a conducting solution. The conductance should, of course, be high to avoid loss of energy due to heat. Aqueous and non-aqueous solutions may be used. Among the more common electrolytes are solutions of sulfuric acid, hydrochloric acid, sodium and potassium hydroxides, and salts of inorganic and organic acids. The nonaqueous media are glacial acetic acid and methyl alcohol.

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[32] Harbaugh and Mathers, *Trans. Electrochem. Soc.*, **64**, 293 (1933).

[33] Gale and Shore, Chemical Engineering Senior Project, University of Illinois, 1939.

[34] Blum and Hogaboom, *Principles of Electroplating and Electroforming.* 2nd ed., McGraw-Hill, New York, 1930, p. 306.

[35] Kalmus, Harper, and Savell, *Trans. Am. Electrochem. Soc.*, **27**, 114 (1915).

[36] C. G. Fink, *private communication*, from the Department of Chemical Engineering, Columbia University.

It should be pointed out that in carrying out electrolytic reductions sulfuric acid is less corrosive in contact with an alundum cup than hydrochloric acid, and that in alkaline reductions a catholyte containing the salt of an alkali metal, such as potassium acetate, is less corrosive than potassium hydroxide.

In addition to the conductors themselves small quantities of salts and other compounds are sometimes added to promote reduction or oxidation (see section on factors influencing reduction and oxidation, pages 168–169 and 200). Promoters of the reduction are: salts of copper, titanium, tin, lead, vanadium, molybdenum, arsenic and antimony oxides, and ketones. Promoters of oxidation are oxidizing agents such as potassium ferricyanide.

C. DIAPHRAGMS

In most of the preparations to be described in this chapter a divided cell must be used. The cathode is separated from the anode in order to prevent the reduced product from being reoxidized or vice versa. Separation of the electrolyte into anolyte and catholyte may be conveniently accomplished by placing one electrode within a porous cup with the other on the outside. The porous cup should have thin walls so that it will absorb a minimum of the organic material. It should, furthermore, be resistant to acid or alkali. Alundum cups have proved satisfactory, but other materials may be used. Cups vary in height from about 33 to 210 mm. and in inside diameter from about 11 to 90 mm. The thickness varies with the size of the cup, from about 1.5 to 10 mm.

The porous diaphragm should offer as little resistance as possible to the diffusion of inorganic ions, but as much as possible to the diffusion of the organic compound undergoing reaction. If the cup is too porous and permits too great a loss of organic material, the pores may made smaller by filling them with some suitable material. The porosity of a cup may be tested by filling it to the top with water and allowing it to leak into an empty beaker. If a cup holding about 150 cc. leaks more than about 1 cc. per hour, it should be treated to reduce pore size. The treatment depends on whether an acid or an alkaline electrolyte is to be used.

In the case of an *acid electrolyte* such as sulfuric acid a modification of a procedure used by Hales[37] is recommended. The cup is allowed to soak in a 20% solution of sodium silicate (water glass) for 1 hour. It is then removed from the sodium silicate solution and placed in a 20% solution of sulfuric acid in which it is allowed to stand for 1 hour. Silicic acid is, thus, deposited in the pores. The cup is then removed from the sulfuric acid and allowed to dry for about 3 hours. At the end of that time it is replaced in a 20% solution of sulfuric acid where it is kept. For decreasing the porosity of cups to be used in *alkaline solutions* the cup is allowed to soak in a 20% solution of magnesium sulfate for 1 hour. It is then transferred to a beaker containing a 10% solution of sodium hydroxide where it is allowed to soak for 1 hour. At the end of that period it is allowed to dry for several hours. The free alkali is then washed out by allowing the cup to soak for an hour or more in successive batches of distilled water until the distilled water is no longer alkaline to litmus. The cup is then placed in the electrolyte which is to be used for the experiment.

It was found by S. W. Briggs in this laboratory several years ago that the efficiency of an electrolytic operation may be markedly affected if the pores of the cup are not filled with the electrolyte to be used in the reaction. He found in the electrolytic reduction of benzophenone that if the pores of the cup were not filled with the catholyte, aqueous alcoholic potassium acetate, the anolyte, 40% potassium carbonate diffused through the cup and caused separation of the benzophenone from solution, thus impairing contact of the benzophenone with the cathode. Another advantage of having the pores of the cup filled with electrolyte is that the loss of organic compound by absorption in the walls of the cup is minimized.

When cups become discolored by organic matter, they can often be cleaned by being soaked in successive portions of an organic solvent for an hour or more. Acetone, for example, has proved effective for this purpose. If the cup still remains discolored, a 20% solution of nitric acid at 60°C. is usually effective. The acid must, of course, be washed out of the pores after the cleaning.

Certain cups contain appreciable amounts of iron, which may be removed by allowing the cup to soak in successive portions of 20% sulfuric acid for several hours until a qualitative test of the sulfuric acid for iron is negative. Other metallic ions, if present in the walls of the cup, may be removed in the same manner.

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[37] R. A. Hales, *private communication*, from the Atlas Powder Co.

After use with cathodes which may be attacked by acids or alkali, the solutions in which the cups are allowed to stand should be tested qualitatively for the metal of the cathode before being used with other cathodes, as it is possible that some metallic ions might be absorbed. If this is the case, the cup should be cleaned with sulfuric acid as previously described.

2. Placing of Electrodes

When solid electrodes are used, the working electrode should, for most economical operation, be surrounded by the other electrode or it should be placed between two of the other electrodes which are connected to each other. For example, if a reduction is to be carried out the anode should surround the cathode or two connected anodes should be placed on either side of the cathode. Current will, thereby, be distributed over the whole cathode surface. If the anode were on one side of the cathode, on the other hand, most of the current would flow only to the side nearest the anode. For the most uniform distribution of current, the working electrode should be equidistant at all points from the other electrode.[38] If a wire gauze or other very porous electrode is used as the working electrode, however, the current will probably be distributed uniformly with the anode on one side. Such an arrangement is advantageous when the maintenance of a low temperature is desirable as the portion of the electrolyte containing the working electrode may be placed in the outer compartment of a two-compartment cell directly in contact with the cooling bath, as shown in Figure 2.

3. Contact between Electrode and Organic Compound

Unless an intermediate is being prepared electrochemically to react with an organic compound, there must be contact between the organic compound and the working electrode. One of the limitations of the electrolytic method for carrying out organic reactions is the insolubility of most organic compounds in aqueous solutions and consequent restriction of diffusion of the compound to the electrode. Several methods are available to facilitate contact.

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[38] Fichter, *Organische Elektrochemie.* Steinkopff, Dresden, 1942, p. 13. Lithoprinted by Edwards, Ann Arbor, 1946.

Certain compounds, although insoluble in water, become soluble by forming salts with the conductor in the electrolyte. Phenols, for example, are soluble in alkaline electrolytes and amines, in acid electrolytes.

In carrying out electrolytic reductions many organic compounds may be brought into aqueous solution by adding varying amounts of a soluble organic compound such as one of the lower alcohols, usually ethyl alcohol, to the catholyte (see section on examples of reduction, page 170). If this procedure is followed in oxidations the solubilizing compound will be oxidized along with the organic compound which it is desired to oxidize. In certain cases nonaqueous solutions may be used, as has been previously stated. Usually their conductance is not as high as that of aqueous solutions. All of these are, of course, susceptible to oxidation at the anode.

It was found by McKee and co-workers that organic compounds will dissolve to appreciable extents in concentrated solutions of salts of aromatic sulfonic acids. These solutions have been used both in reduction and oxidation of organic compounds.[39–41]

Organic compounds need not necessarily be in solution in the electrolyte, but may be suspended and sometimes emulsified by vigorous stirring. It may be possible to use surface active agents to assist in emulsification.[42]

For operations with small amounts of organic solids the material has been made into a paste with powdered carbon or graphite and pressed into a perforated anode or cathode.[43–45]

4. Procedure

In carrying out electrolytic reactions the following conditions must be considered: the concentration of the conducting acid, base, or salt, the concentration of the organic compound, the current density, the

[39] McKee and Brockman, *Trans. Electrochem. Soc.*, **62**, 203 (1932).

[40] McKee and Heard, *ibid.*, **65**, 301, 327 (1934).

[41] McKee and Gerastopolou, *ibid.*, **68**, 329 (1935).

[42] Bjorksten, *ibid.*, **88**, 95 (1945).

[43] Nithack German Pat. 123,554 (1901).

[44] Chaumat, Brit. Pat. 19,027 (1907).

[45] White and Lowy, *Trans. Electrochem. Soc.*, **62**, 223 (1932).

temperature near the working electrode, the agitation, the current concentration, and finally the duration of the reaction.

The effect of the *concentration of the conductor* in the solution and the amount of organic compound to be used will be discussed under special headings later.

The *current density* may be varied by changing the size of the electrode with constant current or by keeping the size of the electrode constant, and changing the amount of current. If the *current concentration* is allowed to increase above a certain point, the temperature of the bath will rise.

Best results are sometimes attained by *heating* or *cooling* the bath. A very simple method of maintaining temperatures up to about 70°C. is to place the electrolytic cell in a water bath heated by a Bunsen burner. Above 70°C. an oil bath may be used. The temperature will vary over about a 5° range. Another method for maintaining elevated temperatures is to heat the cell, for example, a beaker, electrically by means of resistance wire wrapped around the cell and insulated with plaster of Paris.

Cooling may be carried out easily by placing the cell in a vessel with an outlet near the top and allowing water to flow into the vessel and leave through the outlet. By this means temperatures of 25–30°C. may be maintained. Lower temperatures are attainable by means of an ice or ice–salt bath.

If the space occupied by the working electrode is large compared with that occupied by the electrolyte, *stirring* will not be necessary. In many other cases the use of a mechanical stirrer is advantageous.

The theoretical duration of the reaction may be determined according to the formula in Section III-1. It is sometimes desirable to know the quantity of gas, hydrogen or oxygen, being absorbed during an electrolysis. A *gas coulometer* is set up according to Figure 3A with electrodes of nickel and the anolyte and catholyte a 15% solution of potassium hydroxide. The gas to be measured is evolved from the electrode in the porous cup into a Hempel buret through a three-way stopcock. The quantity of exit gas from the cell, measured in the same manner, may be compared with that from the coulometer.[46,47]

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[46] Müller-Ellingham, *A Laboratory Manual of Electrochemistry*. Routledge, London, 1931.

[47] Arndt, "Elektrochemische Methoden," in Houben-Weyl, *Methoden der organischen Chemie*. Vol. II, Thieme, Leipzig, 1925.

IV. REACTIONS AT THE CATHODE

1. Reduction

The greatest number of electro-organic syntheses have been carried out by electrolytic reduction. It is more flexible than other operations because the number of available electrodes is greater and the choice of electrolytes, wider.

A. CONTROLLING FACTORS

In order to obtain optimum conversions and yields of reduction products a number of factors must be taken into account, as indicated above in Section II-4.

Composition of the Catholyte. The composition of the catholyte often determines the direction of the reduction. This is particularly true of changes in *p*H. In an acid catholyte nitrobenzene is reduced to aniline as the final product, while in alkaline solution the products are the bimolecular azoxy-, azo-, or hydrazobenzene[48] because of the reaction between the intermediate nitroso compound and hydroxylamine to form the azoxy compound. In acid solution the main product of the reduction of benzophenone at the active single metal cathodes is benzopinacol, while in alkaline solution it is benzohydrol.[49]

Not only is the acidity or alkalinity important, but also the concentration of the conductor in the catholyte. Methyl propyl ketone is reduced to pentane at a cadmium cathode in higher yields in a catholyte of 30% sulfuric acid than in one containing 20 per cent of the acid.[50] Higher yields of benzohydrol are obtained when benzophenone is reduced in a catholyte of 30% potassium acetate than in one of lower concentration. Resin formation in the walls of the porous cup was observed at a concentration of 10% potassium acetate.

Cathode Material. The rate and extent of reduction and sometimes the type of product will depend on the nature of the cathode material. It has been stated in Section II-2-D that, in general, more complete and rapid reductions are obtained at cathodes of high hydrogen overvoltage. In many instances, however, the hydrogen overvoltage is not the deciding factor. In the electrolytic reduction of nitrobenzene to aniline, excellent yields are obtained at a cathode of nickel wires in a catholyte of hydrochloric acid.[51] Cadmium, zinc, lead, and mercury are active cathodes for the reduction of methyl propyl ketone to pentane.[52] Tin and aluminum, both cathodes of high hydrogen overvoltage, are practically inactive. Benzoic acid is reduced to benzyl alcohol only at cathodes of lead and cadmium,[53] and *N*,*N*-dimethylvaleramide to *N*,*N*-dimethylamylamine, only at lead of the eleven cathodes studied.[54]

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[48] Haber, *Z. Elektrochem.*, **4**, 506 (1898).

[49] Swann, Briggs, Neklutin, and Jerome, *Trans. Electrochem. Soc.*, **80**, 163 (1941).

[50] Swann, *ibid.*, **62**, 177 (1932).

The yields of product may differ markedly even at active cathodes of high hydrogen overvoltage. The best yield of benzyl alcohol in the electrolytic reduction of benzoic acid is 85% at a lead cathode. The best at cadmium was about 60% even after the passage of three times the theoretical amount of current. The reduction evidently begins to be inhibited in the latter part of the run. It is suggested that, when sufficient benzyl alcohol is formed, it is adsorbed by the cathode in preference to the benzoic acid and that reduction ceases.

A change in the medium in which a reduction is carried out may effect the yield at a given cathode and also the type of product. When methyl propyl ketone is reduced in glacial acetic acid containing concentrated sulfuric acid, the yields of pentane at the same cathodes are of the same order of magnitude, but lower than those obtained in aqueous solution. This relation holds with most electrode materials. However, a tin electrode is as active as some of the other cathodes of high hydrogen overvoltage.[55] In the electrolytic reduction of benzophenone in aqueous sulfuric acid appreciable yields of the pinacol are obtained only at mercury and aluminum cathodes.[49] Most of the cathodes studied are inactive. In glacial acetic acid, on the other hand, reaction takes place at all cathodes, but the purest product—in this case benzopinacoline—is obtained at an iron cathode.[56]

It should be pointed out that in aqueous solutions, also, the activity of a cathode depends on the medium. It has been stated that most cathodes are inactive in acid solution for the reduction of benzophenone. In alkaline solution, on the other hand, many of the cathodes are active and excellent yields of benzohydrol are obtained.[49]

[51] Otin, *Z. Elektrochem.*, **16**, 674 (1910).
[52] Swann and Feldman, *Trans. Electrochem. Soc.*, **67**, 195 (1935).
[53] Swann and Lucker, *ibid.*, **75**, 411 (1939).
[54] Swann, *ibid.*, **84**, 165 (1943).
[55] Swann, Deditius, and Pyhrr, *Trans. Electrochem. Soc.*, **68**, 321 (1935).
[56] Swann, *ibid.*, **64**, 313 (1933).

Physical Structure of Cathode Material. Changes in the physical structure of the cathode material may effect the yield and character of the reduction product.

Cold-Rolling. In the reduction of *p*-nitrophenol to *p*-aminophenol in alkali the rate of reaction at electrolytic silver was greater than at cold-rolled silver.[57] In this laboratory poorer yields of pentane from methyl propyl ketone were obtained at cadmium sticks which had been hammered into flat electrodes than at the original sticks themselves. The grain size of the flat sheets was much smaller than that of the sticks.[50] The yields of aniline in the electrolytic reduction of nitrobenzene at a low carbon steel cathode become progressively greater as the steel is subjected to greater strain. When the steel is strained to the point of fragmentation of the crystals, the yield of aniline is lowered.[58] Another factor which may influence the efficiency of a cathode is the orientation of the crystals in the cathode. The yields of benzyl alcohol at extruded lead rod cathodes as received were decidedly higher than those at the same lead after it had been recast.[53] It is possible that some preferred orientation of the crystals had occurred when the lead recrystallized after extrusion. The yields of benzyl alcohol compared favorably with those obtained at lead electroplated from a perchlorate bath.

Casting Temperature. The temperature at which an electrode is cast has been shown to be important. Higher yields of isobutyl alcohol in the reduction of methyl ethyl ketonē have been obtained at a zinc cathode cast in a mold at room temperature than at one cast in a mold at 370°C.[59] This was also true in the reduction of the ketone to butane at cadmium cathodes.

Surface Treatment. Caffeine is easily reducible at the spongy surface of a "prepared" (see page 171) and also at a roughened lead cathode when not reducible at a smooth surface.[60]

The effect of etching has been found to be important. In the electrolytic reduction of benzoic acid to benzyl alcohol a smooth, machined cadmium cathode is inactive, but can be activated by etching the surface either chemically or electrochemically.[53] In the electrolytic reduction of methyl ethyl ketone at a zinc cathode cast in a cold mold, etching caused an increase in the yield of butane with a corresponding decrease in the yield of *sec*-butyl alcohol.[59]

Higher yields of acetophenone pinacol from acetophenone in alkaline solution are obtained at smooth copper cathodes than at electrodes which have been etched in nitric acid.[61] In order to obtain good yields of benzopinacol from benzophenone in acid solution at an aluminum cathode, the aluminum must be etched.[49] Not only is etching necessary, but also an oxide coat of uniform thickness, put on by dipping the cathode in a solution of sodium hydroxide and subsequently using it as anode in a dilute sulfuric acid solution for a short period of time.

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[57] Russ, *Z. physik. Chem.*, **44**, 641 (1903).

[58] Solanki, *Trans. Electrochem. Soc.*, **88**, 97 (1945).

[59] Swann, Benoliel, Lyons, and Pahl, *ibid.*, **79**, 83 (1941).

[60] Tafel, *Z. physik. Chem.*, **34**, 187 (1900).

[61] Swann, Ambrose, Dale, Rowe, Kerfman, and Axelrod, *Trans. Electrochem. Soc.*, **85**, 231, (1944).

Surfaces of lead electrodes are markedly affected by corrosion. A lead electrode which was previously used in the electrolytic reduction of methyl ethyl ketone, during which process it was attacked to form tetraisobutyllead gave very poor results when used for the reduction of benzoic acid.[53] Furthermore, electrolytes containing organic acids or compounds which undergo hydrolysis to form acids are deleterious to the surfaces of lead electrodes. After several runs in presence of benzoic acid[53] and of acetanilide in dilute surfuric acid,[62] large areas of the surfaces of lead cathodes were covered with lead sulfate which caused the cathodes to become inactive. Before reduction the cathodes were "prepared" according to a modification of the procedure of Tafel (see page 171). At the beginning of a run the cathodes were covered with brown lead oxide. It is suggested that the quality of this oxide changes and that it becomes susceptible to attack by the organic acid or by sulfuric acid. The organic salt would be converted to lead sulfate by the sulfuric acid. It was shown that the grain size of the lead itself was smaller than it was before the cathode was used. The change in the character of the lead surface might bring about a difference in the oxide coat.

Liquid and Solid States. Whether a cathode is in the liquid or solid state is apparently important. Cinnamic acid is reduced to β,β-diphenyladipic acid[63] in decidedly higher yields at a liquid than at a solid gallium cathode (Gallium m.p., 42.5°C.).

It was shown in this laboratory that the physical structure of an alloy cathode is important in electrolytic reductions. In a study of the reduction of methyl propyl ketone to pentane at cadmium amalgam cathodes it was found that the yield of pentane was correlated with the melting point diagram of the cadmium–mercury system[64] and that small changes in the percentage composition of the cathode would produce markedly different yields in regions where the physical characteristics of the alloy varied greatly with change in composition. The carburation of a low-carbon steel cathode will cause a decrease in its activity for the reduction of nitrobenzene to aniline in sulfuric acid solution.[58]

The discussion of the influence of the surfaces on the efficiency of reductions was included for readers who are interested in studying the influence of the cathode material and in developing more efficient cathodes. For preparative work as illustrated in the examples given later only the paragraphs on the use of lead cathodes are important.

Current Density. It was stated in Section II-2-C that the hydrogen overvoltage is related to current density. By using a cathode of platinum black at a very low current density, and hence at a low cathode potential, *p*-aminophenol is obtained when nitrobenzene is reduced in acid solution. By increasing the current density aniline is obtained as the main product. In alkaline solution azoxybenzene is obtained at low current densities and hydrazobenzene at higher current densities.[65] The character of the product may, therefore, be changed in certain reactions by changing the current density.

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[62] Swann, *Trans. Electrochem. Soc.*, **84**, 165 (1943).

[63] Wilson, *ibid.*, **75**, 353 (1939).

[64] Swann, Read, and Howard, *Trans. Electrochem. Soc.*, **69**, 345 (1936).

The optimum current density for a given reduction will depend on the organic compound being reduced, the cathode material, the nature of the catholyte, and the desired product.

In the reduction of methyl propyl ketone to pentane,[66] the current density at a cadmium cathode could be varied within wide limits without effect on the yield of pentane. On the other hand, in the reduction of benzophenone to benzohydrol at most cathodes the yields decreased rapidly with increases in current density[67] above 0.02 amp. per cm.^{2}. In glacial acetic acid the optimum current densities for reduction of methyl propyl ketone to pentane were much higher than in aqueous solution.[68] Naturally, as the current density is increased atomic hydrogen will be formed faster than it can react with the organic compound and only hydrogen ion will accept the electron, permitting unreacted gas to escape (see page 150).

Temperature. In general, the rate of an electrolytic reduction increases with the temperature. This is, however, not always the case. The yield of pentane in the reduction of methyl propyl ketone at a cadmium cathode[69] was only slightly higher at 60°C. than at 30°C.

In certain reactions the purity of the product will be higher at elevated temperatures. This was true in the electrolytic reduction of benzophenone to benzohydrol.[67] If the organic compound to be reduced is easily hydrolyzed—an amide, for example—it will be necessary to carry out the reduction at a low temperature.

Current Concentration. The yield of reduction product may vary with changes in current concentration (see Section III-4).

Effect of Added Compounds. Higher yields of reduction products are sometimes obtained by adding small amounts of certain substances to the catholyte. Copper, zinc, and tin salts if added to a catholyte containing an aromatic nitro compound in acid solution improve the yield of aniline markedly even at cathodes of low hydrogen overvoltage.[70] The metals may be electrodeposited and remove oxygen from phenylhydroxylamine to form aniline, the last step in the reduction, or act catalytically by some other mechanism.[71]

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[65] Haber, *Z. Electrochem.*, **4**, 506 (1898).

[66] Swann, *Trans. Electrochem. Soc.*, **62**, 177 (1932).

[67] Swann, Briggs, Neklutin, and Jerome, *ibid.*, **80**, 163 (1941).

[68] Swann, Deditius, and Pyhrr, *ibid.*, **68**, 321 (1935).

[69] Swann and Field, *Trans. Electrochem. Soc.*, **72**, 327 (1937).

Stannous chloride is a well-known reducing agent for aromatic nitro compounds. After oxidation it is regenerated at the cathode. Many other materials have been added to promote reduction. The use of nickel wires as a cathode in hydrochloric acid for the reduction of nitrobenzene to aniline was mentioned previously.[72] It is possible that this reduction is successful on account of catalysis. The yield of *N,N*-dimethylbenzylamine in the reduction of *N,N*-dimethylbenzamide at a lead cathode in sulfuric acid is greatly increased upon addition of small amounts of arsenic or antimony oxides to the catholyte.[73] An example of the use of an organic compound as a promoter is found in the reduction of 2-nitro-*p*-cymene in strong sulfuric acid to 2-amino-5-hydroxy-*p*-cymene at a Monel metal cathode[74]; aromatic or mixed ketones such as benzophenone or acetophenone increased the yield.

Certain compounds inhibit reductions even in small quantity. Silver or platinum salts stop the reduction of caffeine to desoxycaffeine at a lead cathode[60] and a number of inorganic salts inhibited the reduction of nitro compounds to amines at a copper cathode.[75]

Duration of the Reaction. Some organic compounds undergo reduction readily at high cathode efficiencies so that the reaction is practically complete after the theoretical amount of current has been allowed to pass. Benzophenone may be reduced to benzohydrol at a mercury cathode with 98% current efficiency.[67] On the other hand, to obtain an 85% yield of benzyl alcohol in the reduction of benzoic acid, triple the theoretical amount of current must be allowed to pass.[76]

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[70] Chilesotti, *Z. Elektrochem.*, **7**, 768 (1901).

[71] Glasstone and Hickling, *Electrolytic Oxidation and Reduction*. Chapman & Hall, London, 1935, p. 189.

[72] Otin, *Z. Elektrochem.*, **16**, 674 (1910).

[73] Kindler, *Ber.*, **57**, 773 (1924).

[74] Mann, Montonna, and Larian, *Trans. Electrochem. Soc.*, **69**, 367 (1936).

[75] Bradt and Linford, *ibid.*, **69**, 353 (1936).

[76] Swann and Lucker, *Trans. Electrochem. Soc.*, **75**, 411 (1939).

B. APPARATUS AND PROCEDURE

The types of apparatus which have been used for reductions in this laboratory are shown in Figure 3 on page 155; an apparatus for reduction at solid cathodes is shown in Figure 3A and one for reductions at a mercury cathode, in Figure 3B. Apparatus for electrolytic reactions is more or less standard.

In carrying out electrolytic reductions at solid cathodes the following procedure is recommended. First the catholyte is made up according to specifications. If an acid catholyte is to be used, a solution is made up of the desired concentration of acid, generally sulfuric acid in water or in a nonaqueous solvent with or without water if the organic compound is insoluble in water. Mixtures of ethyl alcohol and water are generally used. The ratio of solvent to water may be varied. The anolyte should be a 10% solution of sulfuric acid except with nonaqueous solutions where water should not diffuse into the catholyte. Stronger solutions when heated give off vapors which cause sneezing and coughing. If the reduction is to be carried out in alkaline solution, the catholyte is made up of the desired concentration of sodium or potassium hydroxide or salts in water or in ethyl alcohol, with or without water as in the case of acid solutions. Potassium acetate (calcium- and magnesium-free) is a very satisfactory salt for use in alcohol–water mixtures. It is quite soluble in ethyl alcohol (33 g./100 cc.); concentrated solutions may, therefore, be used. For alkaline reductions an anolyte of 40% potassium carbonate is recommended. Lower concentrations have been found to undergo electroendosmosis through the porous cup and into the catholyte, causing the organic compound in solution in the catholyte to be salted out.

After the catholyte and anolyte solutions have been made up, the porous cup to be used should be placed in a position in the catholyte so that it is completely submerged and allowed to remain there for an hour or more. For use in acid solutions when sulfuric acid is used in both catholyte and anolyte a 20% aqueous solution of sulfuric acid is used for the treatment of the cup.

When the experiment is to be started, the rubber stopper into which the cathodes have been fitted is attached to the outlet of the reflux condenser so that the tip of the condenser is flush with bottom of the rubber stopper. In this way the gases evolved during electrolysis will not be trapped under the rubber stopper where they would revent contact between the catholyte and the cathode.

The surfaces of all solid single metal cathodes except thin electroplates (for lead, see below) are cleaned by anodization. For experiments in acid solution the cathode is placed in the center of a beaker containing a solution of 20% sulfuric acid. The acid should cover the cathode completely. An aluminum sheet is placed around the cathode which is now connected to the positive side of the source of current with the aluminum connected to the negative side. Current is turned on for two minutes at an anode current density of 0.02 amp. per cm.^{2}. In this laboratory the cathodes for study are all 100 cm.^{2} and a current of 2 amp. is, therefore, used. The current is then turned off, the bath removed, and the cathode washed thoroughly with distilled water. For alkaline solutions the same procedure is followed except that the anodization is carried out in a 10 per cent sodium hydroxide solution with a copper sheet surrounding the cathode. Anodization in sulfuric acid has also been carried out.

A lead cathode is "prepared" by a modification of the Tafel[77] method no matter whether it is to be used in acid or in alkaline solution. The cathode to be used is placed as before in a 20% solution of sulfuric acid surrounded by a sheet of lead. The cathode is used as anode under the conditions described above except that the current is allowed to flow for five minutes. A layer of chocolate brown lead oxide forms on the surface of the lead used as anode. The polarity is reversed and the current again allowed to flow for five minutes. The lead oxide is reduced to spongy metallic lead. The cycle is repeated. At the end of the second cycle a third is begun, but the cathode is left in the oxidized condition. It is washed thoroughly with distilled water before being used in the reduction.

After the anodization or "preparation" of the cathode, the porous cup to be used is taken out of the *catholyte*. A weighed or measured quantity of the *organic compound* to be reduced and any promoter are placed in the cup into which there is immediately poured sufficient catholyte to fill completely the space left in the cup after it has been attached to the rubber stopper holding the cathodes and after the desired temperature is reached. If a run is to be carried out at an elevated temperature, allowance should be made for expansion of the catholyte. The amount of organic compound used is 10 to 20% of the total catholyte by weight.

The cup containing the catholyte is fitted snugly to the rubber stopper with the cathodes. A beaker containing the anode is put into its proper position with the anode surrounding the cup which rests on the bottom of the beaker. For aqueous acid solutions a sheet of lead is used as the anode and for carbonate anolytes, one of iron. A platinum anode is used with nonaqueous anolytes.

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[77] Tafel, *Ber.*, 33, 2209 (1900).

The *anolyte* is now poured quickly into the anode compartment so that the liquid levels of anolyte and catholyte are the same.

The *current* is turned on and adjusted quickly to the desired value. The water bath is rapidly heated (Section III-4) until the catholyte has reached the desired temperature and is then adjusted to maintain constant temperature. The amperage is reread in case any adjustment is necessary. In runs at low temperatures the whole cell is lowered into the bath of running water which may be fed from the water outlet of the reflux condenser. Sometimes an ice bath is used. If the run lasts for several hours, current and temperature should be read once an hour and adjusted if necessary. With long runs at high currents (5 amp. or more) in acid solution, higher concentrations of sulfuric acid are recommended to keep sufficient acid in the catholyte for good conductivity. Long runs in alkaline solution are not recommended on account of undesirable diffusion unless anolyte and catholyte are solutions of alkalis.

At the end of the run the porous cup containing the catholyte is detached from the rubber stopper as soon as possible and the contents poured into a beaker. Cathode and cup are washed with distilled water, or in certain cases with organic solvents, to remove the adherent organic material and the washings are added to the catholyte in the beaker. The porous cup is again placed in a portion of 20% sulfuric acid or catholyte as described in Section III-1-C. If the catholyte is not immediately removed from contact with the cathode, the cathode may be corroded. Furthermore, if the catholyte is allowed to stand in the porous cup, some may be lost by diffusion.

The operation of the mercury cell is similar except that the catholyte is outside the porous cup. The latter is filled with anolyte up into the connecting tube which is used as a sight glass. Water should be poured into the anolyte at frequent intervals to replace that lost by electrolysis. The anode in both acid and alkaline reductions is a stout platinum wire (about No. 18) and several inches in length. It is conveniently used in the form of a coil.

The products are recovered by the usual procedures of organic chemistry.

The procedure for carrying out electrolytic reductions is illustrated by two preparations described below.

Electrolytic Reduction of Benzoic Acid to Benzyl Alcohol: Figure 3, Apparatus A (page 155). *Anode:* lead sheet. *Anolyte:* 10% sulfuric acid in a 400-cc. beaker. *Cathode:* commercial lead sheet (99.9%) 7.7 × 3 × 0.3 cm.; total area 51.7 cm. *Catholyte* in porous cup about 85 cc. of a solution consisting of 20 cc. of water, 50 cc. of ethyl alcohol, and 40 grams of sulfuric acid. *Dimensions of porous cup:* 100 mm. in height, 47 mm. inside diameter, 3 mm. in thickness. *Weight of benzoic acid:* 20 grams.

After the lead cathode (see page 171) is activated the cell is set up and the beaker lowered into a cooling bath. Water is allowed to flow through the reflux condenser and thence to the cooling bath. A current of 5 amp. is allowed to flow through the cell for 10.5 hours. The cathode current density is 0.1 amp. per $cm.^2$.

At the end of the run the current and water are shut off, the porous cup disconnected, and its contents poured into an 800-cc. beaker. The cup is washed with water and the washings added to the catholyte in the beaker. The catholyte is neutralized with solid sodium carbonate thereby salting out a layer containing benzyl alcohol in ethyl alcohol. The layer is separated from the catholyte and refluxed with 15 grams of sodium hydroxide for 1 hour to saponify any esters. After the saponification the alcoholic liquid is subjected to steam distillation until the distillate is no longer turbid. The distillate is then salted out with potassium carbonate until dry and is then distilled until the temperature of the thermometer reaches 120°C. The neutralized catholyte and residue of steam distillation are both extracted with ether and the extract added to the crude benzyl alcohol in the distilling flask, after drying overnight with anhydrous magnesium sulfate. The ether is driven off and the residual benzyl alcohol is weighed. The weight is 14 g. or a yield of 79%. The benzyl alcohol is almost pure and distills at 200–202° (uncorr.).

Electrolytic Reduction of Benzophenone to Benzohydrol: Figure 3, Apparatus B (page 155). *Anode:* About 2 inches of No. 18 platinum wire sealed in glass, which is then filled with mercury (see page 155). *Anolyte:* 40% potassium carbonate in porous cup 79 mm. in height, 27 mm. inside diameter, and 1.5 mm. in thickness attached to a 14 mm. glass tube by a rubber stopper. The liquid level should be in the tube and water should be added during the electrolysis to maintain it. *Cathode:* mercury, 100 cm. in area, covering the floor of a 1-liter, wide-mouth Erlenmeyer flask; the top of the flask is cut off and the new opening shaped to receive a No. 12 rubber stopper; two side arms for the thermometer and electrical connection to the mercury (see page 163). *Catholyte:* 100 cc. of a solution of 400 g. of potassium acetate, 680 cc. of ethyl alcohol, and 70 g. of water. *Weight of benzophenone:* 20 g.

The cell is set up as shown in the diagram and the flask placed in a heating bath (see page 163). The tube with the porous cup is set in the rubber stopper so that the cup will be submerged in the catholyte to a point just above but not touching the mercury. A current of 2 amp. is turned on and the flask heated quickly until the temperature of the catholyte is 80 to 85°C. The current is allowed to flow for three hours.

At the end of this period the current and heat are shut off and most of the catholyte decanted into sufficient water to precipitate benzohydrol and any unchanged benzophenone. The mercury and residual catholyte are poured into a separatory funnel from which the mercury is drawn off and the supernatant liquid added to the main body of catholyte. Alcohol is added to the separatory funnel and the mercury poured back and drawn off again. The alcoholic solution is added to the main body of the catholyte which is allowed to stand until solidification of the product is complete. The product is then filtered off and recrystallized from petroleum ether, b.p. 60–68°C. The weight is 19.69 or 97% yield of material, m.p. 64–65° or 65–66°C.

It may be advantageous to carry out the reduction of certain nitro compounds to amines chemically with stannous chloride. If the recovery of the amine from the stannic chloride is difficult, the separation may be accomplished electrochemically by placing in the mixture a thick carbon rod as cathode and a small porous cup containing a thick carbon rod as anode in a solution of 2 *N* sulfuric acid. For a solution containing 100 g. of stannous chloride and 120 cc. of concentrated hydrochloric acid, a current of 2 amp. is used. Tin is deposited on the cathode. The current is shut off when the evolution of hydrogen is strong. The separation may be run overnight.[78]

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[78] Gatterman-Wieland, *Laboratory Methods of Organic Chemistry.* Macmillan, New York, 1937, p. 317.

C. EXAMPLES

A number of electrolytic reductions of organic compounds have been carried out in yields which compare favorably with those by other methods. Discussion of these and other reactions is based on reviews[79-81]* by the present author and will be referred to as I,[79] II,[80] and III,[81] respectively, with table and page numbers attached. This method of reference is used throughout the chapter. In using these reviews the errata and additions should be consulted.

$$RNO_2 + 6\,H^+ + 6\,F \rightarrow RNH_2 + 2\,H_2O$$

Nitro compounds, both aromatic and aliphatic have been reduced electrolytically to amines in a large number of cases in 53 to 100% yields.[82-84] Better yields of methyl *m*-aminobenzoate,[83] 93 to 95%, have been obtained catalytically.[85] Most of the catholytes have been aqueous or aqueous alcoholic solutions of sulfuric or hydrochloric acids. In most of the reductions promoters have been added: cupric chloride, titanium chloride, stannous chloride, molybdic acid, and vanadyl sulfate. The acid concentration should not be too high or rearrangement of the intermediate phenylhydroxylamine to *p*-aminophenol or derivatives will take place. The following cathodes have been used: nickel (sheet, wires, and gauze), lead, lead electroplate, copper (sheet and gauze), mercury, and carbon (solid and porous). The nitro group is easily reduced and it has been possible, with certain compounds containing it and another reducible group, to obtain the amine without reduction of the second group, provided that insufficient current for the reduction of both is allowed to pass. Thus the nitro group has been reduced in preference to the following: arsonic acid, carboxyl group in aromatic esters, and pyridine ring. It should also be pointed out that in the case of picric acid one nitro group is apparently more easily reduced than the others, with the result that it is possible to prepare a dinitro amine.

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[79] Swann, *Trans. Electrochem. Soc.*, **69**, 287 (1936). (I)

[80] Swann, *ibid.*, **77**, 459 (1940). (II)

[81] Swann, *ibid.*, **88**, 103 (1945). (III)

* Reprints are obtainable from the Engineering Experiment Station, Engineering Hall, University of Illinois, Urbana, Illinois. The pagination of Reprint No. 6 (Review No. I) differs from that of the original paper in *Trans. Electrochem. Soc.* References to Review No. I may be located in Reprint No. 6 by referring to the bottom of p. 498 in Reprint No. 19 or in Review No. II.

[82] I, Table IX, p. 298.

[83] II, Table IX, p. 467.

[84] III, Table IX, p. 106.

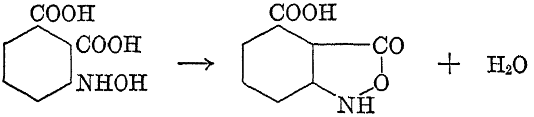
[85] Ungnade and Henick, *J. Am. Chem. Soc.*, **64**, 1737 (1942).

o-Nitrophenol is reduced to *o*-aminophenol[86] even in alkaline solution due to the fact that the *o*-nitrosophenol rearranges to the oximinoquinone which is reduced to the aminophenol.

The work of Weiss and Reiter[82] was on *o*-nitro-α-toluenesulfonic acid. Nitro compounds may also be reduced to amines by a stannous chloride solution. The resulting stannic chloride may be separated from the amine electrolytically (see page 174).

$$C_6H_5NO_2 + 4\,H^+ + 4\,F \rightarrow p\text{-}HOC_6H_4NH_2 + H_2O$$

Reduction of *aromatic nitro compounds* to *p-aminophenols*[87, 88] was discovered by Gattermann[89, 90] in 1893 and the method he used has been named for him. A smooth platinum cathode is used in concentrated sulfuric acid. At this cathode, reduction of the hydroxylamine does not proceed rapidly to the amine and in the presence of the concentrated sulfuric acid it rearranges to the *p*-aminophenol. A carbon cathode has also been used with benzophenone as a promoter. Recently *p*-aminophenol has been prepared from nitrobenzene in 73% yield on a pilot plant scale at a Monel metal cathode in the presence of mercury and cerium salts.[91] The yields of *p*-aminophenols vary from 55.5 to 83%.



An isolated example of the reduction of *aromatic nitro compounds* to *phenylhydroxylamines*[92] is that of 3-nitrophthalic acid at a smooth platinum cathode in sulfuric acid solution; the yield is quantitative. The hydroxylamino group as soon as it is formed reacts with the adjacent carboxyl group to form a 1,2-dihydro-2-ketoanthranil.

$$RCH{=}CRNO_2 + 8\,H^+ + 8F \rightarrow RCH_2CHRNH_2 + 2\,H_2O$$

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[86] I, Table IX, p. 299.

[87] I, p. 300.

[88] II, Table IXA, p. 470.

[89] Gattermann, *Ber.*, **26**, 1844 (1893).

[90] Gattermann and Koppert, *Chem.-Ztg.*, **17**, 210 (1893).

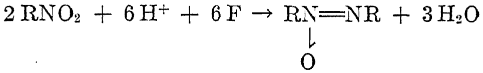
[91] Dey, Govindachari, and Rajagopolan, *J. Sci. Ind. Research* (*India*), **4**, 574 (1946).

[92] II, p. 470.

A number of *2-aminoethyl compounds* have been prepared in 20 to 91% yields by the reduction of *α,β-unsaturated nitro compounds*.[93–95] Most of the nitrostyrenes were reduced at a lead cathode in hydrochloric acid solution, while the nitropropenyl compounds were reduced at a mercury cathode in a solution of sulfuric acid in glacial acetic acid, alcohol, and water. Better yields[93] of α-methylphenethylamine, 50 to 55%, have been obtained from phenylacetone and formamide.[96] *p*-Methoxy-α-methylphenethylamine has been prepared in better yield, 68.6%, by the reduction of *p*-methoxybutyrophenone oxime with sodium amalgam.[97] A nickel amalgam cathode has also been effective in alcohol–acetic acid–sulfuric acid for the preparation of 2-furanethylamine. The desirability of the electrolytic method for carrying out these reactions is stressed by Slotta and Szyszka.[94]

$$O_2NC_6R_4CH{=}CHNO_2 + 14\,H^+ + 14\,F \rightarrow H_2NC_6R_4CH_2CH_2NH_2 + 4\,H_2O$$

Several *amino-2-aminoethyl compounds*[98] have been prepared in 49 to 54% yields by the reduction of *nitro-α,β-unsaturated nitro compounds* at a cathode of lead electroplated on lead. The catholyte contained hydrochloric acid.



$$2\,RNO_2 + 6\,H^+ + 6\,F \rightarrow \underset{\substack{\downarrow\\ O}}{RN}{=}NR + 3\,H_2O$$

A great many aromatic *nitro compounds* have been reduced to the *azoxy stage*.[99–102] The reaction appears to be general except for *o*- and *p*-nitrophenols, and anilines, the *N*- and *N,N*-substituted anilines, and certain hindered nitro compounds which are reduced to amines even in alkaline solution. The yields vary from 11 to 100%. Reduction of nitro compounds to azoxy compounds has in general been carried out by suspending or dissolving the nitro compound in an

[93] I, Table X, p. 301.

[94] II, Table X, p. 471.

[95] III, Table X, p. 107.

[96] Magidson and Garkusha, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 339 (1941).

[97] Savitskii and Makhnenko, *ibid.*, **10**, 1819 (1940).

[98] III, Table XA, p. 108.

[99] I, Table XI, p. 302.

[100] I, p. 339.

[101] II, Table XI, p. 473.

[102] III, Table XI, p. 109.

alkaline catholyte at a nickel cathode. A cathode of low hydrogen overvoltage is used so that the azoxy compound will not be rapidly reduced. Advantage has been taken of the insolubility of the azoxy compound which precipitates from the solution and out of contact with the cathode. For the reduction of the less soluble nitro compounds alcohol is added to the catholyte. In a number of cases lead and mercury cathodes have been used. In one case in which the azoxy compound was soluble good yields were obtained by limiting the amount of current (see page 152).

$$2\,RNO_2 + 8\,H^+ + 8\,F \rightarrow RN{=}NR + 4\,H_2O$$

As in the case of the azoxy compounds a great many *azo compounds* have been prepared by the reduction of *aromatic nitro compounds*.[103–105] The reaction appears to be general except for the types of compounds mentioned above. The yields vary from 23 to 100%. It should be mentioned that in later work the azo compound was not obtained in the reduction of *p*-nitro-*N*,*N*-dimethylaniline.[103–106]

In order to prepare azo compounds the azoxy compounds must be kept in solution for further reduction. This has been accomplished by adding to the catholyte alcohol or salts of aromatic sulfonic acids. It is interesting to note that no electrolytic reductions of nitro compounds of high molecular weight to the azo stage have been reported. A temperature near the boiling point of the catholyte is maintained in order to increase the rate of reaction of the hydrazo compound with the nitro or nitroso compound. Nickel cathodes are most generally used, but phosphor bronze has been used in sulfonate solutions.

Again, as in the reduction in acid solution, the nitro group is easier to reduce than certain others. The acetyl group, for example, remains intact.

The work of Weiss and Reiter[82] was on *p*-nitro-α-toluenesulfonic acid.

$$2\,RNO_2 + 10\,H^+ + 10\,F \rightarrow RNHNHR + 4\,H_2O$$

Hydrazo compounds have been prepared in many cases by the reduction of *nitro compounds* although not as successfully as the

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[103] I, Table XII, p. 304.

[104] II, Table XII, p. 476.

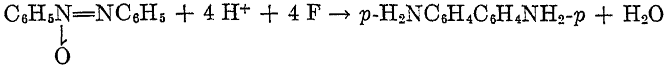
[105] III, Table XII, p. 111.

[106] Rohde, *Z. Elektrochem.*, **7**, 328 (1900).

azoxy compounds.[107–109] The yields vary from 50 to 95%. The nitro compound is reduced under conditions which allow the azo compound to form, *i.e.*, an alkaline bath in which the intermediates are soluble and usually a nickel cathode. The azo compound is then reduced. The reduction is carried out by lowering the current density at the cathode to about one quarter of its previous value. It has been found possible to reduce certain nitro compounds to the hydrazo stage without lowering the current density. Monel metal and lead cathodes have been used in these reductions.

$$RN{=}NR + 2\,H^+ + 2\,F \rightarrow RNHNHR$$

One example is reported of the reduction of an *azo compound* to a *hydrazo compound* in 70% yield[110] but there are many more where nitro compounds have been the starting materials and the azo compound has been the intermediate. The usual nickel cathode was used.



$$C_6H_5\underset{\substack{\downarrow\\ O}}{N}{=}NC_6H_5 + 4\,H^+ + 4\,F \rightarrow p\text{-}H_2NC_6H_4C_6H_4NH_2\text{-}p + H_2O$$

It is possible to reduce *azoxy or azo compounds to* benzidines[111] by using an acid catholyte. The reduction was carried out at a lead cathode in 55 to 60% yield.

$$RNO_2 + 4\,H^+ + 4\,F \rightarrow RNHOH + H_2O$$

Several *aliphatic hydroxylamines*[112] have been prepared in 65 to 80% yields by reduction of aliphatic nitro compounds in an acid catholyte at nickel or electroplated copper cathodes. The lower members of the series were isolated as *p*-nitrobenzaldoximes.

$$R_2NNO_2 + 6\,H^+ + 6\,F \rightarrow R_2NNH_2 + 2\,H_2O$$

$$R_2NNO + 4\,H^+ + 4\,F \rightarrow R_2NNH_2 + H_2O$$

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[107] I, Table XIII, p. 307.
[108] I, p. 340.
[109] II, Table XIII, p. 479.
[110] II, p. 481.
[111] III, p. 112.
[112] I, Table XIV, p. 309.

Hydrazines[113–115] of several types have been prepared in 26 to 95% yields by the reduction of *nitro- and nitrosoamines.* Acid catholytes have been used with lead, mercury, cadmium, copper, and galvanized copper cathodes.

$$\text{RCOR} + 4\,\text{H}^+ + 4\,\text{F} \rightarrow \text{RCH}_2\text{R} + \text{H}_2\text{O}$$

Carbonyl groups in aliphatic ketones with no branched chains on the adjacent carbon atoms have been successfully reduced to *methylene groups*, in 47 to 97% yields.[116, 117] The reaction is usually carried out in sulfuric acid at a cadmium cathode. It has been shown in this laboratory that equally good results may be obtained with cadmium amalgam[118] and zinc[119] cathodes in the reduction of methyl propyl ketone to pentane. An amalgamated zinc cathode was used successfully in the reduction of acetone to propane.[120]

Alicyclic ketones have been reduced to hydrocarbons at cadmium cathodes in sulfuric acid solution.[116]

In order to reduce aromatic ketones to hydrocarbons it is necessary to use amalgamated zinc cathodes.[116] Under these conditions several simple and substituted ketones have been reduced. Along with the carbonyl group in benzoin the hydroxyl group has also been reduced. Better yields, about 90%, of 1-benzylnaphthalene have been obtained with hydrazine as the reducing agent.[121]

$$\text{R}_2\text{CO} + 2\,\text{H}^+ + 2\,\text{F} \rightarrow \text{R}_2\text{CHOH}$$

Carbonyl compounds have been reduced to *alcohols* in 48 to 92% yields.[122–127] Aliphatic ketones have been reduced at mercury

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[113] I, Table XV, p. 310.

[114] II, Table XV, p. 482.

[115] III, Table IX, p. 106.

[116] I, Table XVI, p. 312.

[117] II, Table XVI, p. 483.

[118] Swann, Read, and Howard, *Trans. Electrochem. Soc.*, **69**, 345 (1936).

[119] Clapp, *Thesis*, University of Illinois, 1940.

[120] E. Müller, *Z. Elektrochem.*, **33**, 253 (1927).

[121] Borsche, Hofmann, and Kühn, *Ann.*, **554**, 23 (1943).

[122] I, Table XVII, p. 314.

[123] I, p. 340.

[124] I, pp. 341, 342.

[125] II, Table XVII, p. 484.

[126] II, p. 485.

[127] III, p. 112.

cathodes in alkaline solution. Aromatic aldehydes have been reduced at lead and copper cathodes in acid and alkaline solution. The reduction of glucose to sorbitol and mannitol has been carried out on a full plant scale using an alkaline catholyte and an amalgamated lead cathode.

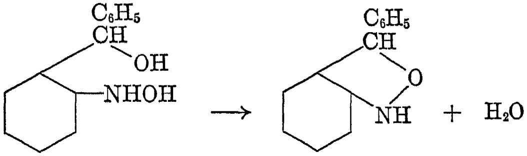
Benzophenone has been reduced to benzohydrol in excellent yield at a mercury cathode. 4-Keto-3-methyl-1-phenyl-5-pyrazolone has been reduced at a lead cathode in an acetic acid solution containing sodium bisulfite.

A better yield, 75%, of 2-methyl-2,4-pentanediol has been obtained by catalytic hydrogenation[128] and of valerolactone, 81.5%, by reduction with sodium amalgam.[129] Also, a higher yield of *p*-methylbenzyl alcohol,[124] 90%, has been obtained from *p*-tolualdehyde and formaldehyde.[130]

$$O_2NC_6H_4CHO + 8\ H^+ + 8\ F \rightarrow H_2NC_6H_4CH_2OH + 2\,H_2O$$

By allowing sufficient current to pass, *m-nitrobenzaldehyde* has been reduced to *m-aminobenzyl alcohol* in acid solution at a lead cathode in 93% yield.[131]

$$o\text{-}O_2NC_6H_4COC_6H_5 + 6\ H^+ + 6\ F \rightarrow o\text{-}HOHNC_6H_4CHOHC_6H_5 + H_2O$$



o-Nitrobenzophenone has been reduced in alkaline solution at a lead cathode to *o-hydroxylaminobenzohydrol*, which immediately loses water to form the *1,2-dihydroanthranil.*[131] The yield is 86%. It should be mentioned that quantitative yields have been reported with aluminum amalgam, the preparation of which is tedious.

$$2\ R_2CO + 2\ H^+ + 2\ F \rightarrow R_2COHCOHR_2$$

Aldehydes have been reduced to *glycols* and *ketones* to *pinacols* in 20 to 73% yields.[132, 133] Michler's ketone has been reduced to the pinacol at a copper cathode in acid solution. Furfural has been reduced to the hydrofuroins at a lead cathode in a catholyte of potassium dihydrogen phosphate to maintain the proper *p*H. Too acidic or too basic a catholyte will cause polymerization of the furfural. Acetone has been reduced to pinacol at a mercury cathode in alkaline solution. This reaction is not general for aliphatic ketones. No pinacol is obtained with either methyl ethyl or di-*n*-propyl ketones. Acetophenone has been reduced to the pinacol in 73% yields at a tin cathode in alkaline solution.[134] Again, this reduction is not general for mixed ketones. It has been possible to obtain the pinacols from *p*-methoxypropiophenone by using a lead cathode in a catholyte of sodium hydroxide in four parts of ethyl alcohol to one part of water.

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[128] Schmerling, Friedman, and Ipatieff, *J. Am. Chem. Soc.*, **62**, 2446 (1940).

[129] Berkenheim and Dankova, *J. Gen. Chem.* (*U. S. S. R.*), **9**, 924 (1939).

[130] *Organic Syntheses*, Coll. Vol. II. Wiley, New York, 1943, p. 590.

[131] I, p. 316.

Where it is applicable the electrolytic method is more convenient for the reduction of carbonyl compounds to glycols and pinacols than chemical methods, involving the preparation of amalgams.

$$RCH{=}CHCOR + 2\,H^+ + 2\,F \rightarrow RCH_2CH_2COR$$

α,β-Unsaturated ketones have been reduced to saturated ketones. Benzylidene ketones have been saturated successfully in alkaline solution at a lead cathode.[131] α,β-Unsaturated aliphatic ketones do not behave in this manner and bimolecular reduction takes place.[135] A quantitative yield of β-phenylpropiophenone has been obtained by catalytic hydrogenation.[136]

$$RCOOH + 4\,H^+ + 4\,F \rightarrow RCH_2OH + H_2O$$

Many *aromatic acids* have been reduced to corresponding *alcohols* in 45–85% yields. Reductions[137–140] are carried out in sulfuric acid solution and rolled lead sheet or lead electroplated from a per-

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[132] I, p. 340.

[133] III, Table XVIIA, p. 113.

[134] Swann, Ambrose, Dale, Rowe, Kerfman, and Axelrod, *Trans. Electrochem. Soc.*, 85, 231 (1944).

[135] Law, *J. Chem. Soc.*, 101, 1544 (1912).

[136] Weidlich and Meyer-Delius, *Ber.*, B74, 1195 (1941).

[137] I, Table XVIII, p. 317.

[138] I. p. 342.

[139] II, Table XVIII, p. 486.

[140] III, p. 114.

chlorate bath are recommended as cathodes. Most of the reductions have been carried out with an aqueous alcoholic catholyte maintained at about 30°C. to prevent esterification of the acid. Benzoic acid has also been reduced to benzyl alcohol in an aqueous sulfuric acid catholyte near the boiling point of the solution. It should be pointed out that aliphatic acids are not reduced under these conditions. *m*-Nitrobenzoic acid has been reduced to *m*-aminobenzyl alcohol.[141] The reduction of ammonium phthalate to phthalide is a special case.

The reduction of aromatic acids to alcohols is difficult to accomplish by methods other than the electrolytic.

$$(COOH)_2 + 4\,H^+ + 4\,F \rightarrow CH_2OHCOOH + H_2O$$

The reduction of *oxalic acid* to *glycolic acid* has been carried out in sulfuric acid solution in 93% yields at a lead cathode.[141]

$$(COOC_2H_5)_2 + 2\,H^+ + 2\,F \rightarrow CHOHOC_2H_5\text{—}COOC_2H_5 + H_2O$$

Ethyl oxalate has been reduced to *ethyl glyoxylate ethyl hemiacetal* in 50% yield.[142] The catholyte was a solution of sulfuric acid in ethyl alcohol and mercury and amalgamated lead cathodes were used. Aqueous solutions did not favor the formation of the glyoxylate.

$$R_2C{=}CRCOOH + 2\,H^+ + 2\,F \rightarrow R_2CHCHRCOOH$$

Many *acids with a double bond* between phenyl and carboxyl or between two carboxyls have been *saturated* in both acid and alkaline solutions.[143–146] The yields vary from 65 to 97%. The reduction appears to be general. In acid solution lead cathodes have been used, while both lead and mercury have been used in alkaline solution. The successful saturation of an ester has also been accomplished. It has been found possible partially to saturate the ring in the reduction of phthalic acid in alkaline solution at a mercury cathode.

$$2\,RCH{=}CHCOOH + 2\,H^+ + 2\,F \rightarrow HOOCCH_2CHRCHRCH_2COOH$$

At a mercury cathode in acid solution certain *cinnamic* acids have been found to undergo bimolecular reduction to the corresponding *adipic acids* in 55% yield.[147] The reduction is not general.[148] The electrolytic method is preferable to the chemical methods, in which amalgams are the reducing agents.

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[141] I, p. 318.
[142] III, p. 114.
[143] I, Table XIX, p. 319.
[144] I, p. 342.
[145] II, Table XIX, p. 487.
[146] III, Table XIX, p. 115.

$$RCONR_2 + 4\,H^+ + 4\,F \rightarrow RCH_2NR_2 + H_2O$$

N and N,N-substituted aliphatic amides and all three types of *aromatic amides* have been reduced to the *corresponding amines* in 10 to 92% yields.[149–151] The catholyte contained sulfuric acid and a lead cathode was used. In the reduction of *N*,*N*-dimethylvaleramide, lead was found to be the only active cathode. Under these conditions the aliphatic amides which are not *N*- or *N*,*N*-substituted are not reduced. The reduction of *p*-aminobenzanilide was attempted at many cathodes without success.[152] As was pointed out earlier it was found that small amounts of arsenic and antimony oxides added to the catholyte in the reduction of certain of the amides would improve the yield of amine. The reductions have been carried out successfully only by the electrolytic method.[150] *N*-Ethyl-*o*-toluidine has been prepared in better yield, 70 to 72%, from *o*-toluidine and ethyl chloride.[153] Also, the yield, 89.4%, of benzylamine[150] by the catalytic hydrogenation of benzaldehyde and ammonia is superior.[154]

$$RCSNR_2 + 4\,H^+ + 4\,F \rightarrow RCH_2NR_2 + H_2S$$

All three types of *phenylthioacetamides* as well as *N-methyl* and *N,N-dimethylthiobenzamide* have been reduced to *amines* in 63 to 100% yields.[155] The unsubstituted thiobenzamide has not been studied. Lead cathodes were used in catholytes of hydrochloric acid. Again, as in the case of the amides the only successful reductions appear to be electrolytic.

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[147] III, Table XIXA, p. 117.

[148] Wilson, *Trans. Electrochem. Soc.*, **88**, 77 (1945).

[149] I, Table XX, p. 320.

[150] II, Table XX, p. 488.

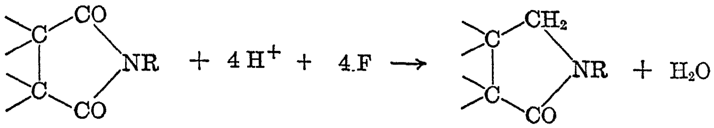
[151] III, Table XX, p. 117.

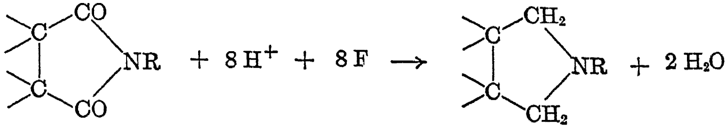
[152] Bresee, *Thesis*, University of Illinois, 1945.

[153] Tolmachev, *Chem. Abstracts*, **29**, 2930 (1935).

[154] Winans, *J. Am. Chem. Soc.*, **61**, 3566 (1939).

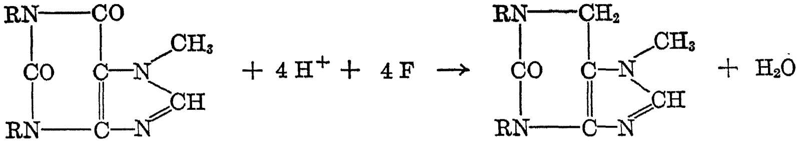
[155] I, Table XXI, p. 322.





Reduction of *amides of dibasic acids* to *cyclic amides* and *amines* has been carried out in 5–80 and 1–57% yields, respectively.[156, 157] Reductions were carried out in acid solution as in the case of the amides. A number of cathodes have been used. Lead is the one most generally used, but cadmium was found to be the best in the reduction of the phthalimides and amalgamated zinc, in the reduction of certain others. A better yield of tetrahydroisoquinoline[156] has been obtained by the catalytic hydrogenation of isoquinoline.[158] Also, the yield of pyrrolidine, 47%, by the catalytic hydrogenation of pyrrole is superior.[159] *Cyclic amides* have been reduced to the corresponding *amines* in sulfuric acid solution at lead and cadmium cathodes.[160–162] Hexahydro-3-pyrrolo[1,2-α]pyrrol-3-one has been reduced to the pyrrole in 35% yield at a lead cathode in sulfuric acid solution.[163]

Two examples of the reduction of cyclic thioamides to amines have been reported.[164, 165] In both reductions a lead cathode was used in a sulfuric acid solution.



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[156] I, Table XXII, p. 324.

[157] II, Table XXII, p. 489.

[158] Cromwell and Cram, *J. Am. Chem. Soc.*, **65**, 301 (1943).

[159] Signiaigo and Adkins, *J. Am. Chem. Soc.*, **58**, 709 (1936).

[160] I, p. 327.

[161] I, p. 330.

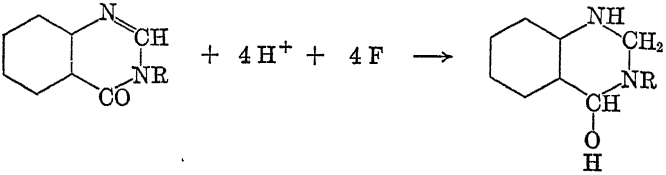
[162] II, pp. 491 and 494.

[163] Galinovsky and Reichard, *ibid.*, **B77**, 138 (1944).

[164] I, p. 329.

[165] II, p. 492.

The reduction of *ketopurines* to *desoxyketopurines* has been carried out in 60 to 70% yields at a lead cathode in sulfuric acid solution.[124, 160, 166]



The reduction of quinazolone to tetrahydroquinazolol is a special case of the *saturation* of a *carbon-nitrogen double bond* and reduction of the carbonyl group of a cyclic amide.[160] The reaction takes place in 42% yield in alkaline solution at a cathode of platinum black electrodeposited on copper. Under these conditions the carbonyl group was reduced to the hydroxy stage.

$$R_2C{=}NOH + 4\,H^+ + 4\,F \rightarrow R_2CHNH_2 + H_2O$$

Both *aldoximes* and *ketoximes* have been reduced to *amines* in 42 to 95% yields.[166, 167] The yield of benzohydrylamine,[167] 87%, by catalytic hydrogenation is superior.[168] The reductions were carried out in sulfuric acid solution at lead and tin cathodes.

$$R_2C{=}NR + 2\,H^+ + 2\,F \rightarrow R_2CHNHR$$

Reductions of *Schiff's bases* to *amines* have been carried out in alkaline solution at lead cathodes in 45 to 90% yields.[169] The bases reported were all derived from ketones.

$$RCNHOC_2H_5 + 4\,H^+ + 4\,F \rightarrow RCH_2NH_2 + C_2H_5OH$$

A number of *benzylamines* have been prepared by the reduction of *imino esters* in 66 to 84% yields.[161] For the preparation of benzylamine see page 184. A catholyte of sulfuric acid was used with a lead cathode.

$$R_2C{=}CRNHR + 2\,H^+ + 2\,F \rightarrow R_2CHCHRNHR$$

A number of examples of the *saturation* of *carbon-carbon bonds*

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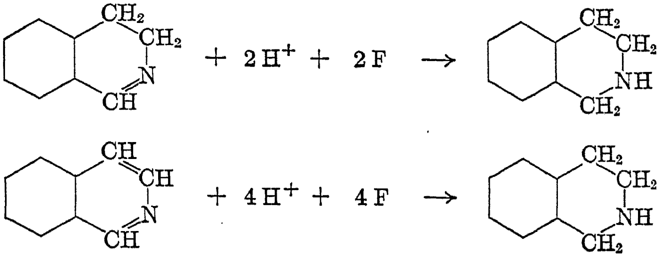
[166] II, p. 491.

[167] I, Table XXIII, p. 328.

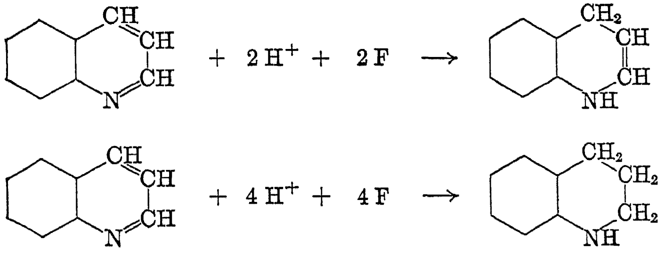
[168] Paul, *Bull. soc. chim.*, 4, 1121 (1937).

[169] II, Table XXIIIA, p. 492.

adjacent to nitrogen have been reported in the carbazole and isoquinoline series.[124, 161, 170, 171] The reductions were carried out at lead cathodes in sulfuric acid solution. The yields are 44 to 100%.



Reductions of *carbon-nitrogen double bonds* in isoquinoline compounds have been carried out at lead cathodes in sulfuric acid solutions in 44 to 70% yields.[170, 171] Papaveriniummethyl chloride has been reduced to laudanosine[170] in better yield, 90%, by cadmium–zinc amalgam.[172] The saturation of the carbon-carbon bond in the second example is similar to the reaction previously reported. The compounds reported are in the alkaloid series. In one instance a phenylazo group attached to an isoquinoline ring was removed during the reduction.



The conditions for the reductions of *quinolines* to *dihydro-* and *tetrahydroquinolines* were the same as reported for the isoquinolines: a lead cathode in dilute sulfuric acid. The yields vary from 32 to 44%.[160, 170] Hydroxyl groups of 4-quinolinemethanols were reduced.

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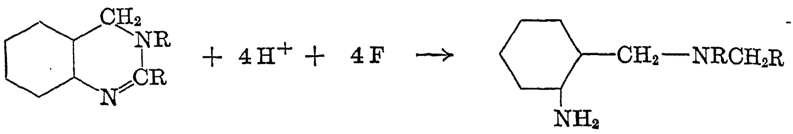
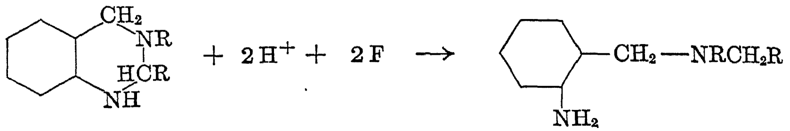
[170] I, Table XXIV, p. 331.

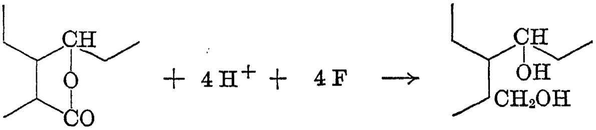
[171] II, Table, XXIV, p. 493.

[172] Awe and Unger, *Ber.*, **B70**, 472 (1937).

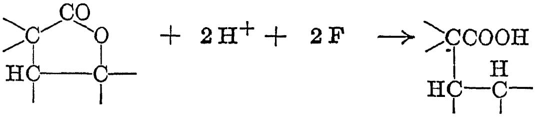




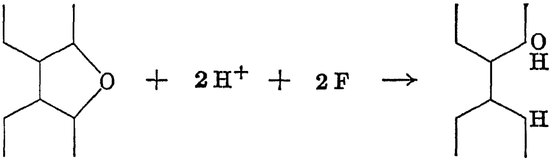
The reduction of *benzodihydropyrimidines* and *scission of the pyrimidine ring* took place in a sulfuric acid solution at a lead cathode.[171] The yields are 56 and 90%, respectively. The carbonyl group of a pyrrolidine ring fused to the pyrimidine ring was reduced to methylene as would be expected.



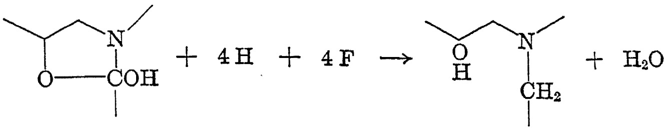
In the alkaloid series *lactones* have undergone *reductive scission* to *hydroxyl groups and primary alcohol groups* in 20 to 25% yield.[170] The reduction was carried out in sulfuric acid solution at a lead cathode.



In another type of alkaloid the lactone was reduced to a carboxyl group in 70% yield. The conditions were the same as before.

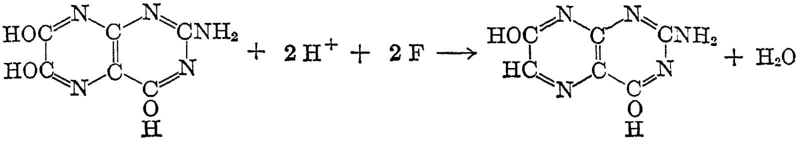


Furane rings in the codeine group have undergone *reductive scission to phenolic hydroxyl groups* in 43.5 to 100% yields at a lead cathode in sulfuric acid solution.[170] Chlorine atoms present in some of these compounds were removed during the reduction.



Very similar to the reductions previously described is that of *vomicine* to *vomicidine*, in 52% yield. A skeleton formula[171] with the reducible groups is shown above. The reduction was carried out in sulfuric acid at a lead cathode.

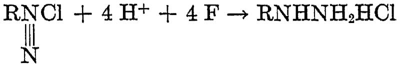
Strychnine and *brucine compounds* have been reduced to *strychnidines*, *brucidines*, and *tetrahydro* derivatives in 23 to 90% yields at a lead cathode in sulfuric acid solution.[171] A mercury cathode has been recommended for the reduction of strychnine on a practical scale.[173]



In the *pteridine* group the reduction of *leucopterin* to the *desoxy* compound has been carried out in 13% yield at a lead cathode in sulfuric acid solution.[174]

$$RN{=}NOH + 4\,H^+ + 4\,F \rightarrow RNHNH_2 + H_2O$$

A number of *diazotates* have been reduced to *hydrazines* in 47 to 100% yields in alkaline solution at a mercury cathode.[175]



$$\underset{\underset{N}{|||}}{RN}Cl + 4\,H^+ + 4\,F \rightarrow RNHNH_2HCl$$

2,4-Xylenediazonium chloride has been reduced to the *hydrazine* in 50% yield in a catholyte containing sodium bisulfite at a tin cathode.[176]

$$RCCl_3 + 2\,H^+ + 2\,F \rightarrow RCHCl_2 + HCl$$

An isolated example of the reduction of *aliphatic trichloro compounds* to *dichloro compounds* has been reported.[177] The catholyte

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[173] Zwicker and Robinson, *J. Am. Chem. Soc.*, **64**, 790 (1942).

[174] III, p. 118.

[175] I, Table XXV, p. 336.

[176] II, Table XXV, p. 497.

[177] II, p. 498.

TABLE II
Electrolytic Reductions

Reactions	Cathode	Catholyte	Promoter	Page
$—NO_2 \rightarrow —NH_2$	Pb, Pb on Pb, Hg, Cu, Ni, C	H_2SO_4, HCl	Cu, Ti, Sn, VO_2 salts, MoO_3	175, 176
$o\text{-}HOC_6H_4NO_2 \rightarrow —NH_2$	Cu	NaOH		176
$C_6H_5NO_2 \rightarrow p\text{-}HOC_6H_4NH_2$	Pt, C, Monel metal	Strong H_2SO_4	$C_6H_5COC_6H_5$, Hg and Ce salts	176
$C_6H_5NO_2 \rightarrow —NHOH$	Pt	H_2SO_4		176
$—CH{=}CHNO_2 \rightarrow —CH_2CH_2NH_2$	Pb, Hg, Hg–Ni	H_2SO_4, HCl		176, 177
$2\,—NO_2 \rightarrow —\underset{\substack{\downarrow\\ O}}{N}{=}N—$	Ni (also Pb and Hg)	Alkali		177, 178
$2\,—NO_2 \rightarrow —N{=}N—$	Ni, phosphor bronze	Alkali		178
$—N{=}N— \rightarrow NHNH—$	Ni	Alkali		179
$2\,—NO_2 \rightarrow —NHNH—$	Ni, Monel metal, Pb	Alkali		178, 179
$C_6H_5\underset{\substack{\downarrow\\ O}}{N}{=}NC_6H_5 \rightarrow p\text{-}H_2NC_6H_4—C_6H_4NH_2\text{-}p$	Pb	Acid		179
$RCH_2NO_2 \rightarrow —NHOH$	Ni, Cu on Cu	Acid		179
$R_2NNO_2 \rightarrow —NH_2$	Pb, Hg, Cd, Cu	Acid		179, 180
$R_2NNO \rightarrow —NH_2$	Fe, Cu			
$RCH_2COCH_2R \rightarrow RCH_2CH_2CH_2R$	Cd, Hg–Zn, Zn	H_2SO_4		180
$C_6H_5COC_6H_5 \rightarrow C_6H_5CH_2C_6H_5$	Hg–Zn	H_2SO_4		180

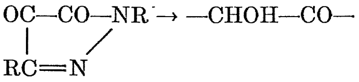
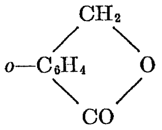
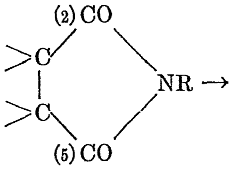
$RCH_2COCH_2R \rightarrow =CHOH$	Pb	Acid and alkali		180, 181
	Hg	Alkali		
$C_6H_5—CHO \rightarrow —CH_2OH$	Pb, Cu	Acid and alkali		181
Glucose → CH_2OH	Pb–Hg	Alkali		181
$C_6H_5COC_6H_5 \rightarrow =CHOH$	Hg	Alkali		181
	Pb	CH_3COOH $NaHSO_3$		181
$O_2NC_6H_4CHO \rightarrow H_2NC_6H_4CH_2OH$	Pb	Acid		181
o-$O_2NC_6H_4COC_6H_5 \rightarrow$ o-$HOHNC_6H_4CHOHC_6H_5$	Pb	Alkali		181
$[p(CH_3)_2NC_6H_4]_2CO \rightarrow =COHHOC=$	Cu	Acid		181, 182
Furfural → $—CHOHHOCH—$	Pb	NaH_2PO_4		181, 182
$CH_3COCH_3 \rightarrow =COHHOC=$	Hg	Alkali		181, 182
$C_6H_5COCH_3 \rightarrow =COHHOC=$	Sn	Alkali		181, 182
p-$CH_3OC_6H_4COC_2H_5 \rightarrow =COHHOC=$	Pb	Alkali in C_2H_5OH–H_2O (4:1)		181, 182
$C_6H_5CH=CHCOR \rightarrow —CH_2CH_2CO—$	Pb	Alkali		182
$C_6H_5—COOH \rightarrow —CH_2OH$	Pb, Pb on Pb Pb on Cu	H_2SO_4		182, 183
o-$C_6H_4(COONH_4)_2 \rightarrow$ 	Pb			183

TABLE II—*Concluded*

Reactions	Cathode	Catholyte	Promoter	Page
$(COOH)_2 \rightarrow HOCH_2COOH$	Pb	Acid		183
$(COOC_2H_5) \rightarrow C_2H_5OHOHCOOOC_2H_5$	Hg, Hg-Pb	H_2SO_4-C_2H_5OH		183
$C_6H_5CH{=}CHCOOH \rightarrow$ —CH_2CH_2—	Pb Pb, Hg	Acid Alkali		183
o-$C_6H_4(COOH)_2 \rightarrow$ o-$C_6H_8(COOH)_2$	Hg	Alkali		183
2 $RCH{=}CHCOOH \rightarrow HOOCCH_2CHRCHRCH_2COOH$	Hg	Acid		183, 184
$RCONR_2 \rightarrow RCH_2NR_2$	Pb	H_2SO_4	As_2O_3, Sb_3O_3	184
$RCSNR_2 \rightarrow RCH_2NR_2$	Pb	HCl		184
 (2)CO → CH_2 (2)CO and (5)CO → CH_2	Pb, Cd, Zn-Hg	Acid		185
CO → CH_2 in ketopurines	Pb	H_2SO_4		185, 186
—N=CH—NR—CO— → —NHCHNRCHOH—	Pt black on Cu	Alkali		186
$R_2C{=}NOH \rightarrow R_2CHNH_2$	Pb, Sn	H_2SO_4		186
$R_2C{=}NR \rightarrow R_2CHNHR$	Pb	Alkali		186

$RCNHOC_2H_5 \rightarrow RCH_2NH_2$	Pb	H_2SO_4		186
$R_2C{=}CRNHR \rightarrow R_2CHCHRNHR$	Pb	H_2SO_4		186, 187
$—CH{=}CH—CH{=}N— \rightarrow —CH_2CH{=}CHNH—$ and $—CH_2CH_2CH_2NH—$	Pb	H_2SO_4		187
$—NRCHRNHR \rightarrow —NRCH_2R + RNH_2$	Pb	H_2SO_4		188
$R_2CHOCOR \rightarrow R_2CHOH + RCH_2OH$	Pb	H_2SO_4		188
$RCOOR \rightarrow RCOOH + RH$	Pb	H_2SO_4		188
$ROR \rightarrow ROH + RH$	Pb	H_2SO_4		188
Strychnine and brucine	Pb	H_2SO_4		189
$R_2NCHROHOR \rightarrow R_2NCH_2R + ROH$	Pb	H_2SO_4		189
$—COH{=}N— \rightarrow —CH{=}N—$	Pb	H_2SO_4		189
$RN{=}NOH \rightarrow RNHNH_2$	Hg	Alkali		189
$RN{=}NCl \rightarrow RNHNH_2$	Sn	$NaHSO_3$		189
$RCCl_3 \rightarrow RCHCl_2$	Pb, Hg-Zn	HCl		189, 194
$RC{\equiv}CR \rightarrow RCH{=}CHR$	Cu	Alkali		194
$AlkSSAlk \rightarrow 2\ AlkSH$	Pb	H_2SO_4, HCl		194
$ArSSAr \rightarrow 2\ ArSH$	Pt	H_2SO_4, HCl		194
$2\ RAsO(OH)_2 \rightarrow RAs = AsR$ $RAsO(OH)_2 \rightarrow RAsH_2$	Hg, Pb	Acid		194

contained hydrochloric acid and the cathode was lead or amalgamated zinc. In the example reported a pyridine ring in the compound was not reduced. The yield is about 50%.

$$RC{\equiv}CR + 2\,H^+ + 2\,F \rightarrow RCH{=}CHR$$

One example of the reduction of *acetylene compounds* to *ethylene compounds* is given.[178] It takes place in alkaline solution at a copper cathode; the yield is 60%.

$$RSSR + 2\,H^+ + 2\,F \rightarrow 2\,RSH$$

Both *aliphatic* and *aromatic disulfides* have been reduced to mercaptans in 20 to 70% yields.[179, 180] Catholytes of sulfuric and hydrochloric acids have been used. The aliphatic disulfides were reduced at lead cathodes while a platinum cathode was used in the reduction of the aromatic disulfide.

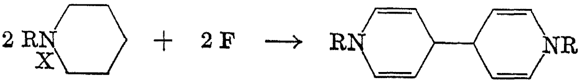
$$2\,RAsO(OH)_2 + 8\,H^+ + 8\,F \rightarrow RAs{=}AsR + 6\,H_2O$$

$$RAsO(OH)_2 + 6\,H^+ + 6\,F \rightarrow RAsH_2 + 3\,H_2O$$

Several examples are given of the reduction of *arsonic acids* to *arseno compounds*, in 55 to 65% yields, and one is given of the reduction to the *arsine*, in 48% yield.[181] Again the reductions were carried out in acid catholytes at mercury and lead cathodes. Whether the arseno compound or the arsine is the final product seems to depend on the acid concentration. High concentrations of acid favor the formation of arseno compounds. It is interesting to note that in the reduction of a chloropyridinearsonic acid dehalogenation took place along with reduction of the arsonic acid, but no reduction of the pyridine nucleus.

2. Coupling

EXAMPLES AND DISCUSSION



One example of the *electrolysis of an alkyl pyridinium halide* and two examples of *electrolysis of alkyl quinolinium halides* are given.[182] Apparently two ions accept two electrons at the cathode to form radicals which couple. The yields are 20 to 50 per cent. Reduction of the pyridine ring does not take place. A cathode of high hydrogen overvoltage is unnecessary. The catholyte is not acidic, but neutral, and conditions are, therefore, favorable to acceptance of electrons by the compound rather than to their acceptance by hydrogen. It has been mentioned previously that the pyridine nucleus is reduced in an excess of sulfuric acid at a lead cathode. Although the optimum conditions for cathodic coupling have not been determined, it would be predicted that a high concentration of organic ions would be favorable, as in anodic coupling to be discussed later.

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[178] III, p. 119.

[179] II, Table XXVIII, p. 497.

[180] III, Table XXVIII, p. 119.

[181] I, Table XXVII, p. 338.

V. REACTIONS AT THE ANODE

1. Electrolysis of Salts of Carboxylic Acids

One of the most useful electrolytic reactions is the coupling at the anode of radicals which are formed when solutions of the salts of carboxylic acids are electrolyzed. The reaction was discovered by Kolbe in 1847 and has been named after him. It is essentially as follows:

$$2\ \mathrm{RCOOM} + 2\ \mathrm{F} \rightarrow 2\ \mathrm{RCOO}\ \text{(anode)} \qquad (1)$$

$$2\ \mathrm{RCOO} \rightarrow \mathrm{R{-}R} + 2\ \mathrm{CO_2} \qquad (2)$$

The first mechanism proposed to explain the reaction was that two organic anions lost two electrons to the anode thus forming radicals which combined as in equation (2). Later Fichter modified the peroxide theory of Schall and suggested that the radicals were formed by oxidation of two molecules of the organic acid at the anode to form a peroxide which decomposed to carbon dioxide and the coupled product:

$$2\ \mathrm{RCOOH} + 2\ \mathrm{OH^-} + 2\ \mathrm{F} \rightarrow (\mathrm{RCOO})_2 + 2\ \mathrm{H_2O} \qquad (3)$$

$$(\mathrm{RCOO})_2 \rightarrow \mathrm{R{-}R} + 2\ \mathrm{CO_2} \qquad (4)$$

The latest theory to explain the Kolbe synthesis is that of Glasstone and Hickling. When the reaction takes place in aqueous solution, they propose that the radicals are formed at the anode due to the reaction of the ions with hydrogen peroxide as the intermediate:

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[182] I, Table XXVI, p. 337.

$$2\,OH^- + 2\,F \rightarrow H_2O_2 \tag{5}$$

$$2\,RCOO^- + H_2O_2 \rightarrow (RCOO)_2 + 2\,OH^- \tag{6}$$

$$(RCOO)_2 \rightarrow R{-}R + 2\,CO_2 \tag{7}$$

When the reaction takes place in nonaqueous solution where hydrogen peroxide is not formed, they propose that the organic anions discharge at the anode as described previously.

A. CONTROLLING FACTORS IN THE KOLBE SYNTHESIS

Composition of Electrolyte. Potassium or sodium salts of organic acids are usually electrolyzed in a cell without a diaphragm. In aqueous solutions high concentrations of the salt are favorable to coupling. In nonaqueous solutions the concentration of the salt has little influence. In general, electrolytes should be kept acidic with the acid of the salt used. Side reactions are promoted in aqueous alkaline electrolytes.

Anode Material. In aqueous electrolytes good yields are obtained only at anodes of smooth platinum. In nonaqueous electrolytes other anodes such as platinum black, gold, or carbon may be used.

Added Compounds. Side reactions are favored by the addition of other salts in aqueous solution. Compounds which catalyze the decomposition of hydrogen peroxide are especially to be avoided.

Current Density. In aqueous solution better yields are obtained at high current densities. In nonaqueous solution the current density is comparatively unimportant.

Temperature. High temperatures do not favor good yields in aqueous solution. In nonaqueous solution the temperature is relatively unimportant.

Duration of the Reaction. The anode current efficiencies are not high and more than the theoretical amount of current is usually necessary.

B. APPARATUS AND PROCEDURE

The apparatus may be similar to that described previously for use in reductions with the exception that no porous cup is used. The anode is a small sheet of smooth platinum so that high current densities are possible without excessive currents. The cathodes are two metal sheets placed a few centimeters away on either side of the anode. The platinum electrodes are made up as described previously (Section III-1-A) and the glass tubes containing the mercury connections are fitted into the rubber stopper holding the reflux condenser. In place of the beaker described under reductions, a tall type is used with a suitably large rubber stopper.

If an aqueous solution is to be electrolyzed, a concentrated solution of the potassium or sodium salt is made up and an equal amount or less of free acid is added to the solution. A cooling bath, as previously described, is placed around the cell. Connections are made and current is allowed to flow until the electrolyte is just alkaline. At that point the current is shut off and the electrolyte poured from the cell into a separatory funnel where the upper layer containing the product is removed. The electrolyte free of product is replaced in the cell, a second charge of fresh acid added, and another run started. A number of runs may be carried out in this way. When the current efficiency begins to fall off, *i.e.*, when the time necessary for the electrolyte to turn alkaline becomes about one and half times as long as in the first run, the electrolyte is discarded and a fresh solution of salt made up. It may be desirable to add ethyl alcohol to the electrolyte to increase the solubility of acids of high molecular weight. Naturally, the procedure is (with obvious changes) also applicable to acetic acid and the formation of ethane.

It is often advantageous with acids of high molecular weight to carry out the electrolysis in nonaqueous solution. A typical procedure is described by Ruzicka and Stoll,[183] using methyl alcohol as the solvent. The salt is dissolved along with free acid and the solution electrolyzed as described above. If the product is insoluble it may be filtered off from time to time. If it is soluble, it is recovered at the end of the run.

C. EXAMPLES OF KOLBE SYNTHESES

$$2\,\mathrm{RCOOM} + 2\,\mathrm{F} \rightarrow \mathrm{R{-}R} + 2\,\mathrm{CO_2}\ \text{(anode)}$$

A number of *aliphatic hydrocarbons*, recently tetratriacontane,[184] have been prepared in 73 to 90% yields[185, 186] The synthesis is, however, not general. Good yields of the coupled product were not obtained when salts of α-substituted aliphatic acids were electrolyzed. Coupling took place only to a small extent when the sodium salt of α-methylbutyric acid was electrolyzed.[187] Good yields of the desired hydrocarbons were not obtained when potassium salts of α-ethylbutyric and α-methylvaleric acids were electrolyzed.[188] While good yields of ethane have been obtained from acetates, the yields of coupled products from certain substituted acetates have been very low or nonexistent. Furthermore, with the exception of acetates, good yields of coupled products are not obtained from the salts of the lower members of the series of aliphatic acids.

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[183] Ruzicka and Stoll, *Helv. Chim. Acta*, **16**, 493 (1933).

[184] Timell, *Svensk Kem. Tid.*, **58**, 67 (1946).

[185] I, Table I, p. 288.

[186] III, Table I, p. 104.

The Kolbe synthesis does not take place in aqueous solution when the double bond is too close to the carboxyl group.[189] Appreciable coupling was not found until the double bond was out as far as the γ-position in a series of six-carbon aliphatic acids. As would be expected aromatic or aliphatic acids with aromatic substituents behave similarly. Coupling did not take place when salts of benzoic or phenylacetic acids were electrolyzed. However in nonaqueous solution 1,4-diphenylbutane was obtained from potassium hydrocinnamate.[190]

$$2\,\mathrm{MOOC(CH_2)_nCOOR} + 2\,\mathrm{F} \rightarrow [\mathrm{(CH_2)_nCOOR}]_2 + 2\,\mathrm{CO_2}\ \text{(anode)}$$

Diesters may be prepared by electrolyzing *salts of acid esters of dibasic acids*.[191-194] This reaction, a form of Kolbe synthesis, was discovered in 1893 and is known as the Crum Brown-Walker reaction. It is carried out in exactly the same manner as the Kolbe synthesis itself. The yields are 5 to 68%; some are based on the salt as starting material where free acid was not used; others are based on free acid in excess of salt.

This reaction has been very useful in the preparation of higher dibasic acids. As might be expected, salts of two acids may be electrolyzed to produce unusual compounds. Just as previously stated, lower yields of coupled products are obtained when methyl groups are substituted in the α-position than in the β-position near the carboxyl group which will be lost.

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[187] Petersen, *Z. Elektrochem.*, **12**, 141 (1906).

[188] Swann, *Trans. Am. Electrochem. Soc.*, **56**, 457 (1929).

[189] Fichter and Holbro, *Helv. Chim. Acta*, **20**, 333 (1937).

[190] Fichter and Stenzl, *ibid.*, **22**, 974 (1939).

[191] I, Table II, p. 289.

[192] I, p. 339.

[193] II, Table II, p. 460.

[194] III, Table II, p. 104.

$$2\,ROCH_2CH_2COOM + 2\,F \rightarrow RO(CH_2)_4OR + 2\,CO_2 \text{ (anode)}$$

Salts of aliphatic acids with alkoxy groups in the β-position or farther from the carboxyl group will undergo Kolbe synthesis successfully to form *diethers*.[194-196] More than one alkoxy group may be present as in salts of acetalic acids. The yields are 50 to 67%.

2. Electrolysis of Salts of Polycarboxylic Esters

EXAMPLES AND DISCUSSION

$$2\,NaCR_3 + 2\,F \rightarrow R_3C{-}CR_3$$
$$R = COOC_2H_5 \text{ or } CN$$

Another type of *anodic coupling* is that involving the anions of *salts of esters*.[197] This is apparently a case of electron transfer at the anode. Platinum anodes have been used. Although the optimum conditions have not been determined, a high concentration of salt would seem desirable. Diethyldicyanobimalonate and hexaethyl ethanehexacarboxylate were prepared in this way in 21 and 40% yields, respectively.

3. Oxidation

A. MECHANISM

Electrolytic oxidation may take place by action of the atomic oxygen formed at the anode. Glasstone and Hickling also propose that the active oxidizing agent may be hydrogen peroxide, as mentioned previously (Section V-1).

B. FACTORS INFLUENCING ELECTROLYTIC OXIDATION

Composition of Anolyte. Similar to reduction, the course of an electrolytic oxidation may depend on the anolyte. Aniline is oxidized to aniline black in acid solution, while azobenzene is the main product in alkaline solution. The lower alcohols are oxidized to aldehydes and

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[195] I, p. 290.
[196] II, Table IIA, p. 461.
[197] II, Table IIB, p. 462.

acids in acid solution; in alkaline solution not only are aldehydes and acids produced, but anodic hydrogen is formed.[198]

Anode Material. As has been pointed out (Sect. III-1-A) the choice of anodes is very narrow. The anodes commonly used in acid solution are smooth platinum, platinum black, and lead oxide. At smooth platinum and lead oxide the overvoltage is so high that the compound in many cases will be oxidized to carbon dioxide and water. Even though the oxygen overvoltage is low at platinum black oxidation to carbon dioxide and water may take place catalytically.[199]

In alkaline solution the anodes commonly used are again smooth platinum and lead oxide, and also iron and carbon. The limitations of these anodes have been discussed previously.

Current Density. When the oxygen overvoltage can be controlled it is possible to obtain intermediate oxidation products at the lower current densities and more complete oxidation at the higher current densities. An example of this is the oxidation of ethyl alcohol to acetaldehyde and then to acetic acid.[200]

Temperature. In general, as would be expected, an increase in the temperature accelerates the oxidation.

Added Compounds. As in the case of reduction a number of compounds may be used to promote oxidation. Reversible oxidizing agents such as ceric sulfate or manganic sulfate have been used; for example, the oxidation of anthracene to anthraquinone[201] may be promoted by the use of these agents, and the oxidation of toluene to benzaldehyde and benzoic acid is markedly promoted by manganic sulfate.[202]

Current Concentration. As in the case of reduction, the yield of oxidation product may be influenced by the current concentration.

Duration of Oxidation. As would be expected, the duration of the reaction depends on the ease of oxidation of the organic compound and on the degree to which the reaction is to be carried.

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[198] Glasstone and Hickling, *Electrolytic Oxidation and Reduction.* Chapman & Hall, London, 1935, p. 342.

[199] Glasstone and Hickling, *loc. cit.*, p. 337.

[200] Glasstone and Hickling, *loc. cit.*, p. 335.

[201] Fontana and Perkin, *Electrochemist and Metallurgist*, **3**, 656 (1904).

[202] Mitchell, *Trans. Am. Electrochem. Soc.*, **56**, 495 (1929).

C. PROCEDURE

Oxidations may be carried out in an apparatus similar to that used for reductions at solid cathodes shown in Figure 3 except that the diaphragm may be omitted. The general technique is also the same. The polarity is, of course, reversed. If the organic compound is not soluble in the electrolyte, a mechanical stirrer is desirable to emulsify it so that contact with the anode will be improved. Blending agents such as acetone and acetic acid have been used to increase the solubility of the organic compound, but the blending agent may itself be oxidized, as was mentioned previously.

For oxidations in acid solution an electrolyte of sulfuric acid is recommended and for oxidations in alkaline solution, sodium or potassium hydroxide. Electrolytes for special purposes will be found in the examples cited.

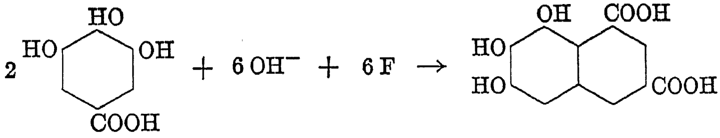
Anodes which may be used have been described on page 200.

If the oxidation products are reducible, the *cathodes* should consist of two small sheets of a metal of low hydrogen overvoltage placed on either side of the anode as described in Section III-2. The two cathodes are small so that the current density will be high enough to bring about the formation of molecular hydrogen.

D. EXAMPLES

$$RCH{=}CHCH_3 + 4\,OH^- + 4\,F \rightarrow RCHO + [CH_3CHO] + 2\,H_2O$$

Several substituted *styrenes* have been oxidized to *aldehydes*[203] at lead oxide anodes in electrolytes containing sodium sulfate, sodium carbonate, or potassium hydroxide. The yields are 52 to 78%.[203a]



Gallic acid undergoes oxidation to form *purpurogallincarboxylic acid* in 35 to 40% yield at a smooth platinum anode in a sodium acetate electrolyte. For a discussion of the mechanism of the oxidation the reader is referred to the work of Willstätter and Heiss.[204]

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[203] I, Table III, p. 291.

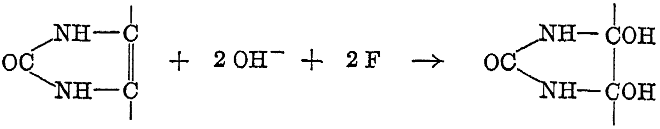
[203a] A better yield of vanillin, 67%, has been obtained by Davies and Hodgson, *J. Soc. Chem. Ind.*, 62, 90 (1943), with sodium dichromate in the presence of sulfanilic acid as the oxidizing agent.

$$1,2,4\text{-}(CH_3O)_3C_6H_3 + 2\ OH^- + 2\ F \rightarrow$$
$$2,4,5\text{-}(CH_3O)_3C_6H_2{-}C_6H_2(OCH_3)_3\text{-}2,4,5 + 2\ H_2O$$

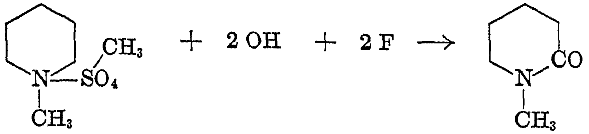
1,2,4-*Trimethoxybenzene* has been oxidized to *2,2′, 4,4′, 5,5′-hexamethoxybiphenyl*[204] in 85% yield in an electrolyte of sodium sulfate and sulfuric acid in aqueous acetone at a lead oxide anode.

$$2\ p\text{-}HOC_6H_4OH + 2\ OH^- + 2\ F \rightarrow p\text{-}O{=}C_6H_4{=}O + p\text{-}HOC_6H_4OH + 2\ H_2O$$

Quinhydrone[205] has been prepared from *hydroquinone* in 75% yield by *oxidation* in sodium sulfate at a carbon anode.



Purine derivatives have been oxidized according to the mechanism shown above.[206] This is the first step and further oxidation, hydrolysis, and condensation may take place. The electrolytes which have been used are lithium carbonate and sulfuric acid, with lead oxide anodes. It is stated that platinum and nickel anodes may be used in the lithium carbonate electrolyte. The yields are 51 to 69%.[206a]



N-Methylpyridiniummethyl sulfate has been *oxidized* to *1-methyl-2-1 pyridol*[207] in the presence of potassium ferricyanide in alkaline solution at an iron anode. This is the electrochemical method of carrying out an oxidation by ferricyanide. The yield is 90%.

$$2\ HNRCSNRH + 2\ OH^- + 2\ F \rightarrow RHNC{=}NRSSRN{=}CNHR + 2\ H_2O$$

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[204] II, p. 461.

[205] III, p. 105.

[206] I, Table IV, p. 292.

[206a] A better yield of tetramethylalloxantin or amalic acid, 81%, has been obtained by Cope, Peck, Eide, and Arroyo, *J. Am. Chem. Soc.*, 63, 356 (1941), with sodium hypochlorite as the oxidizing agent and subsequent addition of stannous chloride.

[207] I, p. 295.

Another type of oxidative coupling is that of *thioureas to formamidine disulfides*.[208] Rearrangement takes place to form a sulfur-sulfur linkage. The oxidation was carried out at platinum gauze anodes in sulfuric acid or perchloric acid electrolytes. The yields are 45 to 96%.

$$R_2S + 2\,OH^- + 2\,F \rightarrow R_2SO + H_2O$$

$$R_2SO + 2\,OH^- + 2\,F \rightarrow R_2SO_2 + H_2O$$

The oxidations of *sulfides* to *sulfoxides* and *sulfones* have been carried out in electrolytes of aqueous acetic acid containing sulfuric acid or hydrochloric acid at anodes of platinum gauze.[209] Both alkyl and aryl sulfides have been oxidized. Yields are 66 to 93%.[209a]

Tribenzylsulfinium sulfate has been prepared in 91% yield from benzyl sulfide.

4. Reactions with Electrolytic Halogen and Thiocyanogen

A. MECHANISM

A number of substitutions and oxidations may be carried out with substances other than oxygen liberated at the anode. Substitutions may take place *directly* by reaction with halogen or cyanogen or *indirectly* in the case of halogens through the intermediate formation of hypohalite. Oxidations are brought about by the hypohalite as oxidizing agent.

B. FACTORS CONTROLLING REACTIONS WITH ANODIC HALOGEN AND CYANOGEN

Composition of Electrolyte. For substitution by thiocyanogen concentrated aqueous solutions of ammonium or alkali thiocyanates have been used. Direct substitution by halogen is usually carried out in halogen acid. Direct substitution of chlorine and bromine has been reported,[210] but direct iodination in hydriodic acid has not been successful. For indirect halogenations or oxidations the electrolyte is always an aqueous solution of the halide.

[208] I, Table V, p. 293.

[209] I, Table VI, p. 294.

[209a] A quantitative yield of ethyl sulfone has been obtained by Böhme and Fischer, *Ber.*, **B75**, 1310 (1942), with ozone as the oxidizing agent.

[210] Glasstone and Hickling, *Electrolytic Oxidation and Reduction*. Chapman & Hall, London, 1935, Chapter 11.

A high concentration of chloride ion is necessary for efficient liberation of chlorine. If the concentration of chloride ion is allowed to diminish seriously, hydroxyl ion will be discharged. The discharge potentials of bromide and iodide ions are far below that for hydroxyl ion and the ions are discharged even from dilute solution.

In indirect halogenation or oxidation where hypohalites are the intermediates, the electrolyte must not be allowed to become too acid or too alkaline because chlorates, bromates, and iodates will then be formed due to side reactions, and the current efficiency for the production of hypohalite will thereby be reduced.

Anode Material. Carbon is the only anode material reported for thiocyanation by electrolysis of thiocyanates. For halogenations, both direct and indirect, smooth platinum has been used. For oxidations with hypobromite carbon anodes have been used.

Current Density. In the electrolysis of chlorides to form hypochlorites high current densities (0.1 amp. per cm.^{2}) have been shown to favor the efficient production of chloroform from ethyl alcohol, but are unnecessary in the formation of hypobromites or hypoiodites.

Temperature. In direct halogenations elevated temperatures increase the rate of reaction between the organic compound and the halogen.

In reactions involving the hypohalites as intermediates low temperatures are desirable for retarding the side reactions involving the formation of halates, but are often impractical on account of the slowness of the reaction of the hypohalite with the organic compound.

Quantity of Current. The amount of current allowed to pass through the solution depends on the optimum concentration of the salt undergoing electrolysis. Current should not be allowed to flow after the concentration of the ion to be discharged at the anode has diminished to a point where oxygen evolution or other side reactions become appreciable.

For direct halogenations the amount of current must be controlled if the monosubstituted product is desired (see Section II-3).

C. PROCEDURE

Thiocyanations and reactions with hypohalites are carried out in undivided cells. In direct halogenations the anode is separated from the cathode by a diaphragm.

The cell may be set up as described in the section on oxidation with the anode (see page 201) in the center or in the porous cup. Any cathode resistant to alkali (or acid) may be used. Nickel sheet is suitable. The anode is carbon or platinum depending on the reaction.

In the preparation of hypohalites for substitution reactions smooth platinum electrodes are used in an electrolyte of the alkali or alkaline earth salt of the halide. The halogen is liberated at the anode and hydrogen at the cathode. The halogen from the anode diffuses toward the cathode, meeting the alkali formed at the cathode and forming the hypohalite which reacts with the organic compound. If sodium or potassium halides are used, the solution must be kept neutral by the addition of carbon dioxide, or of iodine with iodide electrolyte. The latter is reduced to hydriodic acid which neutralizes the alkali. Another method is the use of an auxiliary cathode in a porous cup. In this way not all of the alkali is formed at the main cathode.

If an alkaline earth salt is used, the solution will remain at the pH of the precipitation point of the alkaline earth. No neutralizing agent is necessary. A platinum anode is used, but nickel or copper cathodes are necessary because they do not seem to adsorb calcium hydroxide and thus raise the resistance of the cell.

In most electrochemical oxidations by hypohalites, calcium bromide solution is used as the electrolyte with carbon electrodes. For the details of the process see below.

Some loss of hypohalite is caused by reduction at the cathode. This may be minimized by covering the cathode with parchment paper[211] or by using alkaline earth halides. When the latter are electrolyzed the hydroxide formed prevents reduction at the cathode.

D. EXAMPLES

$$RC_6H_5 + 2\ SCN^- + 2\ F \rightarrow RC_6H_4SCN + [HSCN]$$

Thiocyanates of several aromatic amines and one phenol have been prepared in 21 to 90% yields.[212] The electrolyte was a solution of *ammonium thiocyanate.*

$$C_6H_5CH_2CH_2COOH + 2\ Cl^- + 2\ F \rightarrow m\text{-}ClC_6H_4CH_2CH_2COOH + HCl$$

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[211] Müller-Ellingham, *A Laboratory Manual of Electrochemistry.* Routledge, London, 1931.

[212] II, Table VIIIA, p. 466.

m-Chlorohydrocinnamic[213] *acid* has been prepared in 99% yield at a platinum anode by electrolyzing a solution of hydrochloric acid containing the hydrocinnamic acid.

$$10\,MX + 10\,F \rightarrow 10\,H + 10\,MOH\ (\text{cathode}) + 5\,X_2\ (\text{anode})$$

$$10\,MOH + 5\,X_2 \rightarrow 5\,MOX + 5\,MX + 5\,H_2O$$

$$C_2H_5OH + MOX \rightarrow CH_3CHO + H_2O + MX$$

$$CH_3CHO + 3\,MOX \rightarrow X_3CCHO + 3\,MOH$$

$$X_3CHO + MOH \rightarrow CHX_3 + HCOOM$$

$$HCOOM + MOX + MOH \rightarrow M_2CO_3 + MX + H_2O$$

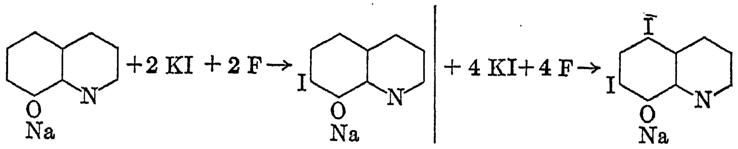
$$6\,MX + 6\,F \rightarrow 6\,H + 6\,MOH\ (\text{cathode}) + 3\,X_2\ (\text{anode})$$

$$6\,MOH + 3\,X_2 \rightarrow 3\,MOX + 3\,MX + 3\,H_2O$$

$$CH_3COCH_3 + 3\,MOX \rightarrow CX_3COCH_3 + 3\,MOH$$

$$CX_3COCH_3 + MOH \rightarrow CHX_3 + CH_3COOM$$

Chloroform has been prepared from *ethyl alcohol* and *iodoform* has been prepared from both *ethyl alcohol* and *acetone*.[214] The current yields (Section II-3) are 92 to 98%. Only one material yield, 99% of chloroform from ethyl alcohol, is reported. A calcium chloride electrolyte was used in preparing chloroform, while sodium and potassium iodides have been used in preparing iodoform. Smooth platinum electrodes were used throughout. The equations show why the electrolyte will gradually become alkaline—hence the necessity for procedures to maintain neutrality.



The iodination of aromatic compounds has been carried out in a divided cell.[213] The starting material was iodinated in an anolyte containing potassium iodide with sodium hydroxide. The yields are 82.4 and 68%.*

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[213] II, Table VIIA, p. 463.

[214] I, Table VII, p. 296.

*A superior yield (92.6%) of 5,7-diiodo-8-quinolinol has been obtained chemically by Zeifman; *Chem. Abstracts*, 34, 3745 (1940).

$$2\,MBr_2 + 4\,F \rightarrow 4\,H + 2\,M(OH)_2\ \text{(cathode)} + 2\,Br_2\ \text{(anode)}$$

$$2\,M(OH)_2 + 2\,Br_2 \rightarrow M(OBr)_2 + MBr_2$$

$$2\,RCHO + M(OBr)_2 \rightarrow 2\,RCOOH + MBr_2$$

$$2\,RCOOH + MCO_3 \rightarrow (RCOO)_2M$$

A great many *aldose sugars* have been oxidized to the corresponding *acids*, in 60 to 100% yields.[215-217] In general a solution of calcium bromide was electrolyzed between carbon electrodes. The oxidation evidently takes place through the intermediate formation of calcium hypobromite. Bromine appears at the anode even when the concentration of bromide is as low as 2%. The acid, as soon as it is formed, reacts with a carbonate, usually calcium carbonate, and is recovered as the salt.

VI. CONCLUSIONS

In this chapter the techniques for carrying out several types of electro-organic syntheses have been described and examples of reactions which have synthetic value have been discussed. The author would like to stress the fact that, while a number of conditions must be fulfilled, electro-chemical syntheses are not difficult to carry out and, furthermore, are not tedious. The experiments need not be watched except for periodic observations and readings of instruments. Runs producing about 100 grams of product may be carried out with standard equipment.

For a selected bibliography of electro-organic reactions, *Organische Elektrochemie* by Fichter is recommended.

Acknowledgment

The source of the material used in the section on general theory was *Principles and Applications of Electrochemistry*, Volume I, by Creighton and Koehler and *An Introduction to Electrochemistry* by Glasstone. Many subjects in the section on apparatus and general procedure have been discussed in the introduction to *Electroorganic Chemistry* by Brockman; *A Laboratory Manual of Electrochemistry* by Erich Müller-Ellingham and *Die Methoden der organischen*

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[215] I, Table VIII, p. 297.

[216] I, p. 339.

[217] II, Table VIII p. 464.

Chemie, Volume II (1925), edited by Houben-Weyl, chapter entitled "Elektrochemische Methoden" by Arndt. *Electrolytic Oxidation and Reduction* by Glasstone and Hickling was the source of the material used in section on the controlling factors of the Kolbe synthesis, of electrolytic oxidation, and of some of the section on the controlling factors in halogenation. *Principles and Practice of Electrochemistry*, Volume II, by Creighton and Koehler and *Organische Elektrochemie* by Fichter were also consulted for material on halogenation. The author desires to express his appreciation to Dr. H. J. Creighton for reviewing the manuscript.

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